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South Wales
NP10 8QQ

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

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Signed Stephen Hordley

Dated 28 November 2003

Patents Form 1/77

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05FEB03 E782376-1 D02093
P01/7700 0.00-0302547.5

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road
Newport
South Wales
NP10 8QQ

1. Your reference

PI-70220P1

2. Patent application number
(The Patent Office will fill in this part)

04 FEB 2003 0302547.5

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

SYNGENTA PARTICIPATIONS AG
Intellectual Property Department
Schwarzwaldallee 215
4058 Basel, SWITZERLAND

08029555001

Patents ADP number *(if you know it)*

If the applicant is a corporate body, give the country/state of its incorporation

4. Title of the invention

Avermectins and Avermectin monosaccharide substituted in the 4'- and 4"-position having pesticidal properties

5. Name of your agent *(if you have one)*

Michael James RICKS

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Syngenta Limited
Intellectual Property Department
Jealott's Hill Research Centre
PO Box 3538, BRACKNELL
Berkshire, RG42 6YA, UNITED KINGDOM

Patents ADP number *(if you know it)*

01282433003

08029571001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

Yes (b)

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	
Description	74
Claim(s)	6
Abstract	1
Drawing(s)	–

10. If you are also filing any of the following, state how many against each item.

Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature: SYNGENTA PARTICIPATIONS AG Joanna Chandler Date 4/2/03.
Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

Joanna Carmen CHANDLER 01344 414079
Julie Anne BOWDICH 01344 414365

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

a) If you need help to fill in this form or you have any questions, please contact the Patent Office on 08459 500505.

b) Write your answers in capital letters using black ink or you may type them.

c) If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.

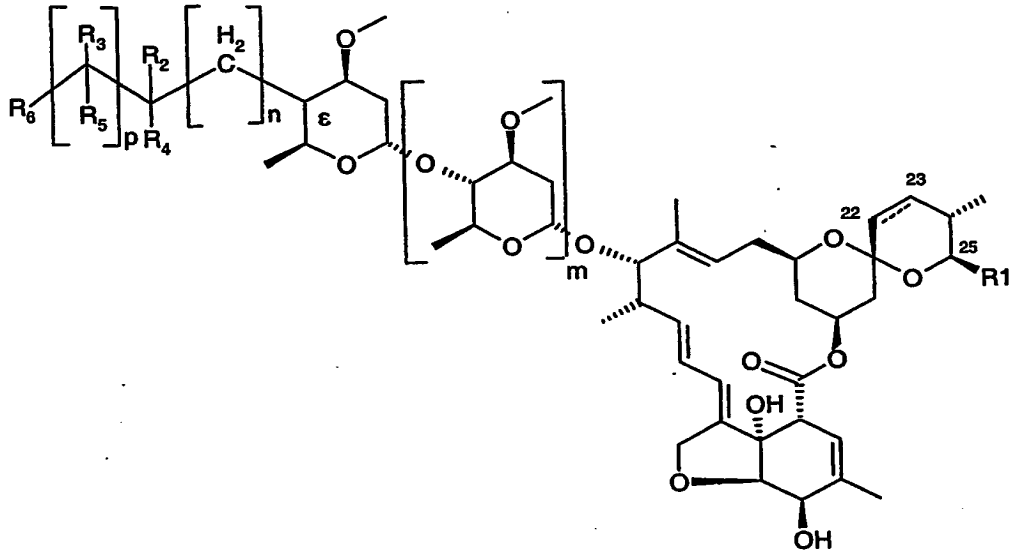
d) If you have answered 'Yes' Patents Form 7/77 will need to be filed.

e) Once you have filled in the form you must remember to sign and date it.

f) For details of the fee and ways to pay please contact the Patent Office.

Avermectins and Avermectin monosaccharides substituted in the 4'- and 4"-position having pesticidal properties

The invention provides (1) a compound of the formula



(I),

wherein the bond of atoms C_{22} and C_{23} is a single or double bond;

m is 0 or 1;

n is 0, 1 or 2;

p is 0 or 1;

R_1 is C_1-C_{12}-alkyl, C_3-C_8-cycloalkyl or C_2-C_{12}-alkenyl;

R_2 is H, C_1-C_{12}-alkyl, C_1-C_{12}-haloalkyl, C_1-C_{12}-hydroxyalkyl, OH, halogen, $-N_3$, SCN, NO_2, CN, C_3-C_8cycloalkyl unsubstituted or substituted by from one to three methyl groups, C_3-C_8halocycloalkyl, C_1-C_{12}alkoxy, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_{12}alkenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_2-C_{12}alkynyl, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy, $-P(=O)(OC_1$-$C_6alkyl)_2$, $-Si(C_1$-$C_6alkyl)_3$, $-(CH_2)$-$Si(C_1$-$C_6alkyl)_3$, $-Si(OC_1$-$C_6alkyl)_3$, $-N(R_9)_2$, $-(CH_2)$-$N(R_9)_2$, wherein the two substituents R_9 are independent of each other, $-C(=X)$-R_7, $-(CH_2)$-$C(=X)$-R_7, $-O$-$C(=X)$-R_7, $-(CH_2)$-O-$C(=X)$-R_7, $-S$-$C(=X)$-R_7, $-(CH_2)$-S-$C(=X)$-R_7, $-NR_9C(=X)R_7$, $-(CH_2)$-$NR_9C(=X)R_7$, $-NR_9NHC(=X)$-R_7, $-NR_9$-OR_{10}, $-(CH_2)$-NR_9-OR_{10}, $-SR_9$, $-S(=O)R_{11}$, $-S(=O)_2R_{11}$; aryl, heterocyclyl, aryloxy or heterocyclyloxy; wherein the aryl, heterocyclyl, aryloxy and heterocyclyloxy

radicals are unsubstituted or, depending upon the possibilities of substitution at the ring, mono- to penta-substituted by substituents selected from the group consisting of OH, halogen, CN, NO_2, SCN, $-N_3$, C_1-C_{12}alkyl, C_3-C_8cycloalkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_8alkenyl, C_2-C_8alkynyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy and phenoxy;

or, when p is 1, R_2 together with R_3 is a bond;

or R_2 together with R_4 is =O or =S;

or R_2 together with R_4 form with the carbon to which they are bound a three- to seven-membered ring, which may be monocyclic or bicyclic, and may be saturated or unsaturated, and that may contain one or two hetero atoms selected from the group consisting of N, O and S, and which is either unsubstituted or independently of one another mono- to pentasubstituted with substituents selected from OH, =O, SH, =S, halogen, CN, $-N_3$, SCN, NO_2, aryl, C_1-C_{12}alkyl, C_3-C_8cycloalkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_8alkenyl, C_2-C_8alkynyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy, phenoxy, phenyl-C_1-C_6alkyl; $-N(R_9)_2$, wherein the two R_9 are independent of each other; C_1-C_6alkylsulfinyl, C_3-C_8cycloalkylsulfinyl, C_1-C_6haloalkylsulfinyl, C_3-C_8halocycloalkylsulfinyl, C_1-C_6alkylsulfonyl, C_3-C_8cycloalkylsulfonyl, C_1-C_6haloalkylsulfonyl and C_3-C_8halocycloalkylsulfonyl; or

or, when p is 0, R_2 together with R_4 and R_6 is $\equiv N$;

or when p is 0, R_2 together with R_6 is $=NOR_9$ or $=NN(R_9)_2$, wherein the two substituents R_9 are independent of each other;

R_3 is H, C_1-C_{12}-alkyl, halogen, halo-C_1-C_2alkyl, CN, $-N_3$, SCN, NO_2, C_3-C_8cycloalkyl unsubstituted or substituted by from one to three methyl groups, C_3-C_8halocycloalkyl, C_1-C_{12}alkoxy, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy-C_1-C_6alkyl, C_3-C_8cycloalkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_3-C_8cycloalkylthio, C_1-C_{12}haloalkylthio, C_1-C_{12}alkylsulfinyl, C_3-C_8cycloalkylsulfinyl, C_1-C_{12}haloalkylsulfinyl, C_3-C_8halocycloalkylsulfinyl, C_1-C_{12}alkylsulfonyl, C_3-C_8cycloalkylsulfonyl, C_1-C_{12}haloalkylsulfonyl, C_3-C_8halocycloalkylsulfonyl, C_2-C_8-alkenyl, C_2-C_8alkynyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy, $-N(R_9)_2$, wherein the two substituents R_9 are independent of each other, aryl, heterocyclyl, aryloxy or heterocyclyloxy; wherein the aryl, heterocyclyl, aryloxy and hetero-

cyclyloxy radicals are unsubstituted or, depending upon the possibilities of substitution at the ring, mono- to penta-substituted by substituents selected from the group consisting of halogen, CN, NO_2, C_1-C_{12}alkyl, C_3-C_8cycloalkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_8alkenyl, C_2-C_8alkynyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyl and C_3-C_{12}haloalkynyloxy;

or when p is 1, R_3 together with R_2 is a bond;

R_4 is H, C_1-C_{12}-alkyl, C_1-C_{12}-haloalkyl, C_1-C_{12}-hydroxyalkyl, OH, halogen, NO_2, CN, C_3-C_8cycloalkyl unsubstituted or substituted by from one to three methyl groups, C_3-C_8halocycloalkyl, C_1-C_{12}alkoxy, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_6alkoxy--C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_{12}alkenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_2-C_{12}alkynyl, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy, -P(=O)(OC_1-C_6alkyl)$_2$, -Si(C_1-C_6alkyl)$_3$, -(CH_2)-Si(C_1-C_6alkyl)$_3$, -Si(OC_1-C_6alkyl)$_3$, -N(R_9)$_2$, -(CH_2)-N(R_9)$_2$, wherein the two substituents R_9 are independent of each other, -C(=X)-R_7, -(CH_2)-C(=X)-R_7, -O-C(=X)-R_7, -(CH_2)-O-C(=X)-R_7, -S-C(=X)-R_7, -(CH_2)-S-C(=X)-R_7, -NR_9C(=X)R_7, -(CH_2)-NR_9C(=X)R_7, -NR_9NHC(=X)-R_7, -NR_9-OR_{10}, -(CH_2)-NR_9-OR_{10}, -SR_9, -S(=O)R_{11}, -S(=O)$_2R_{11}$; aryl, heterocyclyl, aryloxy or heterocyclyloxy; wherein the aryl, heterocyclyl, aryloxy and heterocyclyloxy radicals are unsubstituted or, depending upon the possibilities of substitution at the ring, mono- to penta-substituted by substituents selected from the group consisting of OH, halogen, CN, NO_2, C_1-C_{12}alkyl, C_3-C_8cycloalkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_8alkenyl, C_2-C_8alkynyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy and phenoxy;

or R_4 together with R_2 forms =O or =S;

or when p is 1, R_4 together with R_5 is a bond;

or, when p is 0, together with R_2 and R_6 is ≡N;

R_5 and R_6 independently of each other are H, C_1-C_{12}-alkyl, -N_3, CN, NO_2, OH, SH, halogen, halo-C_1-C_2alkyl, C_3-C_8cycloalkyl unsubstituted or substituted by from one to two methyl groups, C_3-C_8halocycloalkyl, C_1-C_{12}alkoxy, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy-C_1-C_6alkyl, C_3-C_8cycloalkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}haloalkylthio, C_2-C_8alkenyl, C_2-C_8alkynyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy, -P(=O)(OC_1-C_6alkyl)$_2$, -CH_2-P(=O)(OC_1-C_6alkyl)$_2$,

$-Si(OC_1-C_6alkyl)_3$, $-N(R_9)_2$, $-O-N(R_9)_2$, wherein the two substituents R_9 are independent of each other, $-C(=X)-R_7$, $-O-C(=X)-R_7$, $-S-C(=X)-R_7$, $-NR_9C(=X)R_7$, $-NR_9NHC(=X)-R_7$, $-NR_9-OR_{10}$, $-SR_9$, $-S(=O)R_{11}$, $-S(=O)_2R_{11}$, aryl, aryloxy, benzyloxy, $-NR_9$-aryl, heterocyclyl, heterocyclyloxy, $-NR_9$-heterocyclyl, $-CH_2$-aryl, $-CH_2-O$-aryl, $-CH_2-NR_9$-aryl, $-CH_2$-heterocyclyl, $-CH_2-O$-heterocyclyl and $-CH_2-NR_9$-heterocyclyl; wherein the aryl, aryloxy, benzyloxy, $-NR_9$-aryl, heterocyclyl, heterocyclyloxy and $-NR_9$-heterocyclyl radicals are unsubstituted or, depending upon the possibilities of substitution at the ring, mono- to penta-substituted by substituents selected from the group consisting of OH, =O, SH, =S, halogen, CN, NO_2, C_1-C_{12}alkyl, C_3-C_8cycloalkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_8alkenyl, C_2-C_8alkynyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy, phenoxy, methylenedioxy, NH_2, $NH(C_1-C_{12}alkyl)$, $N(C_1-C_{12}alkyl)_2$ and C_1-C_6alkylsulfinyl; or

R_5 and R_6 are, together with the carbon atom to which they are bound, a five- to seven-membered ring, which may be saturated or unsaturated, and which may contain one or two members selected from the group consisting of O, NR_8 and S; and which is optionally substituted with one to three substituents selected from C_1-C_{12}-alkyl, CN, NO_2, OH, halogen, halo-C_1-C_2alkyl, C_3-C_8cycloalkyl C_3-C_8halocycloalkyl, C_1-C_{12}alkoxy, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy-C_1-C_6alkyl, C_3-C_8cycloalkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_3-C_8cycloalkylthio, C_1-C_{12}haloalkylthio, C_2-C_{12}alkenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_2-C_{12}alkynyl, C_3-C_{12}haloalkynyl and C_3-C_{12}haloalkynyloxy;

or when p is 1, R_5 together with R_4 is a bond;

or, when p is 0, R_6 together with R_2 and R_4 is $\equiv N$;

R_7 is H, OH, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_2-C_{12}alkenyl, C_2-C_{12}alkynyl, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy, C_2-C_8alkenyloxy, $-N(R_8)_2$, wherein the two R_8 are independent of each other; aryl, aryloxy, benzyloxy, heterocyclyl or heterocyclyloxy; and wherein the aryl, aryloxy, benzyloxy, heterocyclyl, heterocyclyloxy radicals are unsubstituted or, depending upon the possibilities of substitution at the ring, mono- to penta-substituted by substituents selected from the group consisting of halogen, CN, NO_2, C_1-C_{12}alkyl, C_3-C_8cycloalkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_8alkenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy and C_2-C_8alkynyl;

R_8 is H, C_1-C_6alkyl, which is optionally substituted with one to five substituents selected from the group consisting of halogen, C_1-C_6alkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy, C_2-C_{12}alkenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_2-C_{12}alkynyl, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy, hydroxy and cyano; C_3-C_8-cycloalkyl, aryl, benzyl or heteroaryl; wherein the aryl, benzyl and heteroaryl radicals are unsubstituted or, depending on the possibilities of substitution on the ring, mono- to trisubstituted by substituents selected from the group consisting of OH, halogen, CN, NO_2, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_2-C_{12}alkenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_2-C_{12}alkynyl, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy and C_1-C_{12}haloalkylthio;

R_9 is H, C_1-C_6alkyl, C_1-C_6cycloalkyl, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_{12}alkenyl, C_2-C_{12}alkynyl, benzyl, aryl, heteroaryl;

R_{10} H, C_1-C_6alkyl, which is optionally substituted with one to five substituents selected from the group consisting of halogen, C_1-C_6alkoxy, NO_2, hydroxy and cyano; C_1-C_{12}haloalkyl, C_2-C_{12}alkenyl, C_2-C_{12}haloalkynyl, C_2-C_{12}haloalkenyl, C_2-C_{12}alkynyl, C_3-C_8-cycloalkyl, aryl, benzyl or heteroaryl; wherein the aryl, benzyl and heteroaryl radicals are unsubstituted or, depending on the possibilities of substitution on the ring, mono- to trisubstituted by substituents selected from the group consisting of OH, halogen, CN, NO_2, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_2-C_{12}alkenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_2-C_{12}alkynyl, C_3-C_{12}haloalkynyl and C_3-C_{12}haloalkynyloxy;

R_{11} is H, C_1-C_6alkyl, which is optionally substituted with one to five substituents selected from the group consisting of halogen, C_1-C_6alkoxy, hydroxy and cyano; -$N(R_9)_2$, wherein the two substituents R_9 are independent of each other; C_3-C_8cycloalkyl, C_3-C_8halocycloalkyl, C_2-C_{12}alkenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_2-C_{12}alkynyl, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy, aryl, benzyl or heteroaryl; wherein the aryl, benzyl and heteroaryl radicals are unsubstituted or, depending on the possibilities of substitution on the ring, mono- to trisubstituted by substituents selected from the group consisting of OH, halogen, CN, NO_2, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_2-C_{12}alkenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_2-C_{12}alkynyl, C_3-C_{12}haloalkynyl and C_3-C_{12}haloalkynyloxy;

X is O or S;

or, if appropriate, an E/Z isomer, E/Z isomer mixture and/or tautomer thereof, in each case in free form or in salt form;

a process for preparing these compounds, their isomers and tautomers and the use of these compounds, their isomers and tautomers; pesticidal compositions whose active compound is selected from these compounds and their tautomers; intermediates for the preparation of the said compounds of the formula (I), methods for the preparation of the compounds of the formula (I), and a method for controlling pests using these compositions.

Hereinbefore and hereinafter, the configuration at the ε-position (4'- or 4"-position) may be (S) as well as (R).

The literature proposes certain macrolide compounds for controlling pests. However, the biological properties of these known compounds are not entirely satisfactory, and, as a consequence, there is still a need for providing further compounds having pesticidal properties, in particular for the control of insects and representatives of the order Acarina. According to the invention, this object is achieved by providing the present compounds of the formula (I).

The compounds claimed according to the invention are derivatives of Avermectin. Avermectins are known to the person skilled in the art. They are a group of structurally closely related pesticidally active compounds which are obtained by fermenting a strain of the microorganism Streptomyces avermitilis. Derivatives of Avermectins can be obtained by conventional chemical syntheses.

The Avermectins which can be obtained from Streptomyces avermitilis are referred to as A1a, A1b, A2a, A2b, B1a, B1b, B2a and B2b. The compounds referred to as "A" and "B" have a methoxy radical and an OH group, respectively, in the 5-position. The "a" series and the "b" series are compounds in which the substituent R_1 (in position 25) is a sec-butyl radical and an isopropyl radical, respectively. The number 1 in the name of the compounds means that atoms 22 and 23 are linked by double bonds; the number 2 means that they are linked by a single bond and that the C atom 23 carries an OH group. The above nomenclature is adhered to in the description of the present invention to denote the specific structure type in the not naturally occurring Avermectin derivatives according to the invention which corresponds to the naturally occurring Avermectin. What is for instance claimed according to the invention are derivatives of compounds of the B1 series, in particular mixtures of derivatives of Avermectin B1, especially B1a and B1b, along with derivatives having a single bond between carbon atoms 22 and 23, and derivatives having other substituents in the 25-position, as well as the corresponding monosaccharides.

Some of the compounds of the formula (I) can be present as tautomers. Accordingly, hereinabove and hereinbelow, the compounds of the formula (I) are, if appropriate, also to be understood as including the corresponding tautomers, even if the latter are not specifically mentioned in each case.

The compounds of formula (I) and, where applicable, their tautomers can form salts, for example acid addition salts. These acid addition salts are formed, for example, with strong inorganic acids, such as mineral acids, for example sulfuric acid, a phosphoric acid or a hydrohalic acid, with strong organic carboxylic acids, such as unsubstituted or substituted, for example halo-substituted, C_1-C_4alkanecarboxylic acids, for example acetic acid, unsaturated or saturated dicarboxylic acids, for example oxalic acid, malonic acid, maleic acid, fumaric acid or phthalic acid, hydroxycarboxylic acids, for example ascorbic acid, lactic acid, malic acid, tartaric acid or citric acid, or benzoic acid, or with organic sulfonic acids, such as unsubstituted or substituted, for example halo-substituted, C_1-C_4alkane- or aryl-sulfonic acids, for example methane- or p-toluene-sulfonic acid. Compounds of formula (I) that have at least one acidic group can furthermore form salts with bases. Suitable salts with bases are, for example, metal salts, such as alkali metal salts or alkaline earth metal salts, for example sodium, potassium or magnesium salts, or salts with ammonia or with an organic amine, such as morpholine, piperidine, pyrrolidine, a mono-, di- or tri-lower alkylamine, for example ethylamine, diethylamine, triethylamine or dimethylpropylamine, or a mono-, di- or trihydroxy-lower alkylamine, for example mono-, di- or tri-ethanolamine. Corresponding internal salts may also be formed where appropriate. The free form is preferred. Among the salts of the compounds of formula (I), the agrochemically advantageous salts are preferred. Hereinbefore and hereinafter, any reference to the free compounds of formula (I) or their salts is to be understood as including, where appropriate, also the corresponding salts or the free compounds of formula (I), respectively. The same applies to tautomers of compounds of formula (I) and salts thereof.

Unless defined otherwise, the general terms used hereinabove and hereinbelow have the meanings given below.

Unless defined otherwise, carbon-containing groups contain in each case 1 up to and including 6, preferably 1 up to and including 4, in particular 1 or 2, carbon atoms.

Halogen- as a group per se and also as a structural element of other groups and compounds, such as haloalkyl, haloalkoxy and haloalkylthio - is fluorine, chlorine, bromine or iodine, in particular fluorine, chlorine or bromine, especially fluorine or chlorine.

Alkyl - as a group per se and also as a structural element of other groups and compounds, such as haloalkyl, alkoxy and alkylthio - is, in each case taking into account the number of carbon atoms contained in each case in the group or compound in question, either straight-chain, i.e. methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl or octyl, or branched, for example isopropyl, isobutyl, sec-butyl, tert-butyl, isopentyl, neopentyl or isohexyl.

Cycloalkyl - as a group per se and also as a structural element of other groups and compounds, such as, for example, of halocycloalkyl, cycloalkoxy and cycloalkylthio - is, in each case taking into account the number of carbon atoms contained in each case in the group or compound in question, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl or cyclooctyl.

Alkenyl - as a group per se and also as a structural element of other groups and compounds - is, taking into account the number of carbon atoms and conjugated or isolated double bonds contained in the group, either straight-chain, for example vinyl, allyl, 2-butenyl, 3-pentenyl, 1-hexenyl, 1-heptenyl, 1,3-hexadienyl or 1,3-octadienyl, or branched, for example isopropenyl, isobutenyl, isoprenyl, tert-pentenyl, isohexenyl, isoheptenyl or isooctenyl. Preference is given to alkenyl groups having 3 to 12, in particular 3 to 6, especially 3 or 4, carbon atoms.

Alkynyl – as a group per se and also as a structural element of other groups and compounds - is, in each case taking into account the number of carbon atoms and conjugated or isolated double bonds contained in the group or compound in question, either straight-chain, for example ethynyl, propargyl, 2-butynyl, 3-pentynyl, 1-hexynyl, 1-heptynyl, 3-hexen-1-ynyl or 1,5-heptadien-3-ynyl, or branched, for example 3-methylbut-1-ynyl, 4-ethylpent-1-ynyl, 4-methylhex-2-ynyl or 2-methylhept-3-ynyl. Preference is given to alkynyl groups having 3 to 12, in particular 3 to 6, especially 3 or 4, carbon atoms.

Halogen-substituted carbon-containing groups and compounds, such as, for example, halogen-substituted alkyl, alkenyl, alkynyl, cycloalkyl, alkoxy or alkylthio, can be partially halogenated or perhalogenated, where in the case of polyhalogenation the halogen substituents can be identical or different. Examples of haloalkyl - as a group per se and also as a structural element of other groups and compounds, such as haloalkoxy or haloalkylthio - are methyl which is mono- to trisubstituted by fluorine, chlorine and/or bromine, such as CHF_2 or CF_3; ethyl which is mono- to pentasubstituted by fluorine, chlorine and/or bromine, such as CH_2CF_3, CF_2CF_3, CF_2CCl_3, CF_2CHCl_2, CF_2CHF_2, CF_2CFCl_2, CF_2CHBr_2, CF_2CHClF,

CF_2CHBrF or CCIFCHCIF; propyl or isopropyl which is mono- to heptasubstituted by fluorine, chlorine and/or bromine, such as $CH_2CHBrCH_2Br$, CF_2CHFCF_3, $CH_2CF_2CF_3$, $CF(CF_3)_2$ or $CH(CF_3)_2$; butyl or one of its isomers, mono- to nonasubstituted by fluorine, chlorine and/or bromine, such as $CF(CF_3)CHFCF_3$ or $CH_2(CF_2)_2CF_3$; pentyl or one of its isomers, mono- to undecasubstituted by fluorine, chlorine and/or bromine, such as $CF(CF_3)(CHF_2)CF_3$ or $CH_2(CF_2)_3CF_3$; and hexyl or one of its isomers, mono- to tridecasubstituted by fluorine, chlorine and/or bromine, such as $(CH_2)_4CHBrCH_2Br$, $CF_2(CHF)_4CF_3$, $CH_2(CF_2)_4CF_3$ or $C(CF_3)_2(CHF)_2CF_3$.

Aryl is in particular phenyl, naphthyl, anthracenyl, phenanthrenyl, perylenyl or fluorenyl, preferably phenyl.

Heterocyclyl is understood as being a three- to seven-membered monocyclic ring, which may be saturated or unsaturated, and that contains from one to three hetero atoms selected from the group consisting of N, O and S, especially N and S; or a bicyclic ring-system having from 8 to 14 ring atoms, which may be saturated or unsaturated, and that may contain either in only one ring or in both rings independently of one another, one or two hetero atoms selected from N, O and S; heterocyclyl is in particular piperidinyl, piperazinyl, oxiranyl, morpholinyl, thiomorpholinyl, pyridyl, N-oxidopyridinio, pyrimidyl, pyrazinyl, s-triazinyl, 1,2,4-triazinyl, thienyl, furanyl, dihydrofuranyl, tetrahydrofuranyl, pyranyl, tetrahydropyranyl, pyrrolyl, pyrrolinyl, pyrrolidinyl, pyrazolyl, imidazolyl, imidazolinyl, thiazolyl, isothiazolyl, triazolyl, oxazolyl, thiadiazolyl, thiazolinyl, thiazolidinyl, oxadiazolyl, dioxaborolanyl, phthalimidoyl, benzothienyl, quinolinyl, quinoxalinyl, benzofuranyl, benzimidazolyl, benzpyrrolyl, benzthiazolyl, indolinyl, isoindolinyl, cumarinyl, indazolyl, benzothiophenyl, benzofuranyl, pteridinyl or purinyl, which are preferably attached via a C atom; thienyl, benzofuranyl, benzothiazolyl, tetrahydropyranyl, dioxaborolanyl, or indolyl is preferred; in particular dioxaborolanyl, pyridyl or thiazolyl. The said heterocyclyl radicals may preferrably be unsubstituted or – depending on the substitution possibilities on the ring system - substituted by 1 to 3 substituents selected from the group consisting of halogen, =O, -OH, =S, SH, nitro, C_1-C_6alkyl, C_1-C_6hydroxyalkyl, C_1-C_6alkoxy, C_1-C_6haloalkyl, C_1-C_6haloalkoxy, phenyl and benzyl.

In the context of the present invention, preference is given to

(2) compounds according to group (1) of the formula (I) in which R_1 is isopropyl or sec-butyl, preferably to those in which a mixture of the isopropyl and the sec-butyl derivative is present;

(3) compounds according to group (1) or (2) of the formula (I), in which n is 0;

(4) compounds according to group (1) or (2) of the formula (I), in which n is 1;

(5) compounds according to group (1) or (2) of the formula (I), in which n is 2;

(6) compounds according to anyone of groups (1) to (5) of the formula (I), in which the substituent in the ε-position is $-(CH_2)_n-CR_2(R_4)CR_3(R_5)(R_6)$;

(7) compounds according to anyone of groups (1) to (5) of the formula (I), in which p is 0;

(8) compounds according to anyone of groups (1) to (7) of the formula (I), in which the substituent in the ε-position is $-(CH_2)_n-C(=O)-R_6$ and R_6 is H, C_1-C_{12}-alkyl, OH, SH, halo-C_1-C_2alkyl, C_3-C_8cycloalkyl unsubstituted or substituted by from one to three methyl groups, C_3-C_8halocycloalkyl, C_1-C_{12}alkoxy, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy-C_1-C_6alkyl, C_3-C_8cycloalkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_3-C_8cycloalkylthio, C_1-C_{12}haloalkylthio, C_2-C_8alkenyl, C_2-C_8alkynyl, $-N(R_9)_2$, wherein the two substituents R_9 are independent of each other, aryl, aryloxy, benzyloxy, $-NR_9$-aryl, heterocyclyl, heterocyclyloxy, $-NR_9$-heterocyclyl; or aryl, aryloxy, benzyloxy, $-NR_9$-aryl, heterocyclyl, heterocyclyloxy or $-NR_9$-heterocyclyl that, depending upon the possibilities of substitution at the ring, are mono- to penta-substituted by substituents selected from the group consisting of OH, =O, SH, =S, halogen, CN, NO_2, C_1-C_{12}alkyl, C_3-C_8cycloalkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_8alkenyl, C_2-C_8-alkynyl, phenoxy, methylenedioxy, NH_2, $NH(C_1$-C_{12}alkyl), $N(C_1$-C_{12}alkyl)$_2$ and C_1-C_6alkylsulfinyl;

(9) compounds according to anyone of groups (1) to (7) of the formula (I), in which the substituent in the ε-position is $-(CH_2)_n-C(R_4)=CR_5(R_6)$;

(10) compounds according to anyone of groups (1) to (5) and (7) to (8) of the formula (I), in which R_3 is H or C_1-C_{12}-alkyl;

(11) compounds according to anyone of groups (1) to (6) of the formula (I), in which the substituent in the ε-position is $-(CH_2)_n-C\equiv CR_6$;

(12) compounds according to anyone of groups (1) to (7) of the formula (I), in which R_2 is is H, C_1-C_{12}-alkyl, C_1-C_{12}-hydroxyalkyl, COOH or $-COO-C_1$-C_{12}-alkyl;

(13) compounds according to anyone of groups (1) to (7) and (9) to (12) of the formula (I), in which R_4 is H, C_1-C_{12}-alkyl, C_1-C_{12}-haloalkyl, halogen, NO_2, CN or C_3-C_8cycloalkyl;

(14) compounds according to anyone of groups (1) to (7) and (9) to (13) of the formula (I), in which R_5 together with R_4 is a bond;

(15) compounds according to anyone of groups (1) to (7) and (9) to (14) of the formula (I), in which R_5 is C_1-C_{12}-alkyl, CN, NO_2, OH, halogen, halo-C_1-C_2alkyl, C_3-C_8cycloalkyl C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_2-C_8alkenyl, C_2-C_8alkynyl, -P(=O)(OC_1-C_6alkyl)$_2$, -CH_2-P(=O)(OC_1-C_6alkyl)$_2$, -Si(OC_1-C_6alkyl)$_3$ or -N(R_9)$_2$;

(16) compounds according to anyone of groups (1) to (15) of the formula (I), in which R_6 independently of each other are C_1-C_{12}-alkyl, CN, NO_2, OH, halogen, halo-C_1-C_2alkyl, -P(=O)(OC_1-C_6alkyl)$_2$, -CH_2-P(=O)(OC_1-C_6alkyl)$_2$, -Si(OC_1-C_6alkyl)$_3$, -N(R_9)$_2$, wherein the two substituents R_9 are independent of each other, -C(=X)-R_7, -NR_9C(=X)R_7, -NR_9NHC(=X)-R_7, -NR_9-OR_{10}, -S(=O)R_{11}, -S(=O)$_2R_{11}$, aryl, aryloxy, benzyloxy, -NR_9-aryl, heterocyclyl, heterocyclyloxy, -NR_9-heterocyclyl; and aryl, aryloxy, benzyloxy, -NR_9-aryl, heterocyclyl, heterocyclyloxy and -NR_9-heterocyclyl that, depending upon the possibilities of substitution at the ring, are mono- to penta-substituted by substituents selected from the group consisting of OH, halogen, CN, NO_2, C_1-C_{12}alkyl, C_3-C_8cycloalkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_8alkenyl, C_2-C_8alkynyl, phenoxy, methylenedioxy, NH_2, NH(C_1-C_{12}alkyl), N(C_1-C_{12}alkyl)$_2$ and C_1-C_6alkylsulfinyl;

(17) compounds according to anyone of groups (1) to (16) of the formula (I), in which m is 1;

(18) compounds according to anyone of groups (1) to (16) of the formula (I), in which m is 0;

(19) compounds according to anyone of groups (1) to (18) of the formula (I), in which the bond between atoms C_{22} and C_{23} is a single bond;

(20) compounds according to anyone of groups (1) to (18) of the formula (I), in which atoms C_{22} and C_{23} is a double bond;

(21) compounds according to anyone of groups (3) to (20) of the formula (I), wherein R_1 is cyclohexyl;

(22) compounds according to anyone of groups (3) to (20) of the formula (I), wherein R_1 is 1-methyl-butyl;

(23) compounds according to one of the groups (1) to (22) of the formula (I) in which the configuration at the ε–position is (*R*);

(24) compounds according to one of the groups (1) to (22) of the formula (I) in which the configuration at the ε–position is (*S*);

(25) compounds according to one of the groups (1) to (7) and (21) to (24) wherein the substituent in the ε-position is $-C(=O)R_6$;

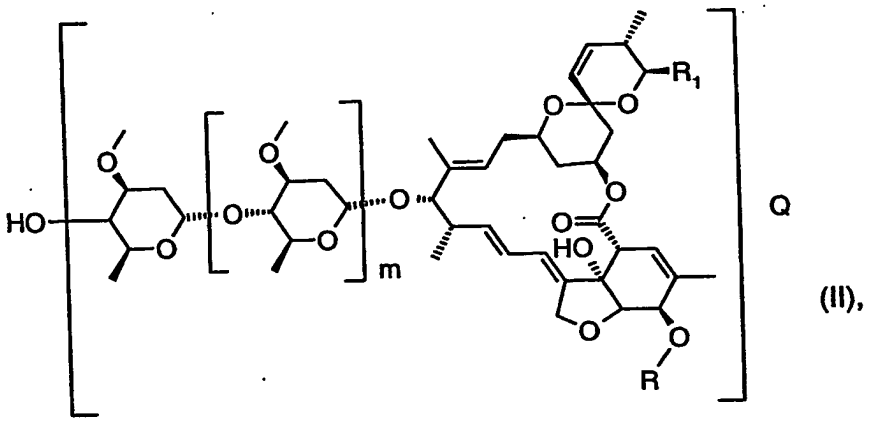
(26) compounds according to one of the groups (1) to (7) and (21) to (25) wherein the substituent in the ε-position is $-CH_2C(=O)R_6$; wherein R_6 is C_1-C_{12}-alkyl, $-N_3$, CN, SH, halogen, halo-C_1-C_2alkyl, C_3-C_8cycloalkyl unsubstituted or substituted by from one to two methyl groups, C_3-C_8halocycloalkyl, C_1-C_{12}alkoxy, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy-C_1-C_6alkyl, C_3-C_8cycloalkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}haloalkylthio, C_2-C_8alkenyl, C_2-C_8alkynyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyl or C_3-C_{12}haloalkynyloxy;

(27) compounds according to one of the groups (1) to (7) and (21) to (25) wherein the substituent in the ε-position is $-CH_2R_6$ or $-CH_2CH_2R_6$ or $-CH_2CH_2CH_2R_6$; and R_6 is OH, C_1-C_6alkyl, C_1-C_{12}alkoxy, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy-C_1-C_6alkyl, C_3-C_8cycloalkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}haloalkylthio, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyloxy, $-N(R_9)_2$, $-O-N(R_9)_2$, wherein the two substituents R_9 are independent of each other, $-O-C(=X)-R_7$, $-S-C(=X)-R_7$, $-NR_9C(=X)R_7$, $-NR_9NHC(=X)-R_7$, $-NR_9-OR_{10}$, $-SR_9$, $-S(=O)R_{11}$, $-S(=O)_2R_{11}$, aryl, aryloxy, benzyloxy, $-NR_9$-aryl, heterocyclyl or heterocyclyloxy.

In the context of the invention, particular preference is given to the compounds of the formula (I) listed in the tables and, if appropriate, to their E/Z isomers and E/Z isomer mixtures.

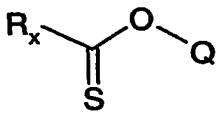
The invention also provides a process for preparing the compounds of the formula (I) and, if appropriate, tautomers thereof, wherein R_1 to R_6 have the same meanings as given above under (1) for formula (I), and m is 0 or 1, n is 1 and p is 0 or 1, characterized in that

(A) a compound of the formula



(II),

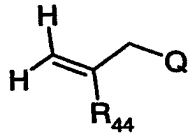
and which is known or can be prepared according to known procedures, wherin R_1 and m have the meanings as given in formula (I) and R is a protecting group, is converted into a compound of the formula



(III),

wherein R_x is imidazolyl, aryloxy, thioalkyl or thioaryl and Q has the same meaning as the part of the formula (II) which is in the bracket marked with Q;

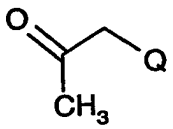
(B) the said compound of the formula (III) is converted into a compound of the formula



(IIa);

wherein R_{44} is H, C_1-C_6alkyl, -Si(C_1-C_6alkyl)$_3$, -(CH_2)-Si(C_1-C_6alkyl)$_3$, -Sn(C_1-C_6alkyl)$_3$, -C(=O)R_7, R_7 is as defined under formula (I), and Q has the meaning as given above in formula (II);

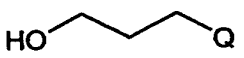
(C) the said compound of formula (IIa) may – provided R_{44} is H - further be converted into a compound of the formula



(IIb),

wherein Q has the meanings as defined above in formula (II); or

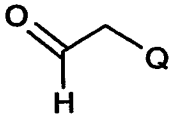
(D) the compound of the formula (IIa) is converted into a compound of the formula



(IIc),

wherein Q has the meanings as defined above in formula (II); or

(E) the compound of the formula (IIa) as defined above is converted into a compound of the formula

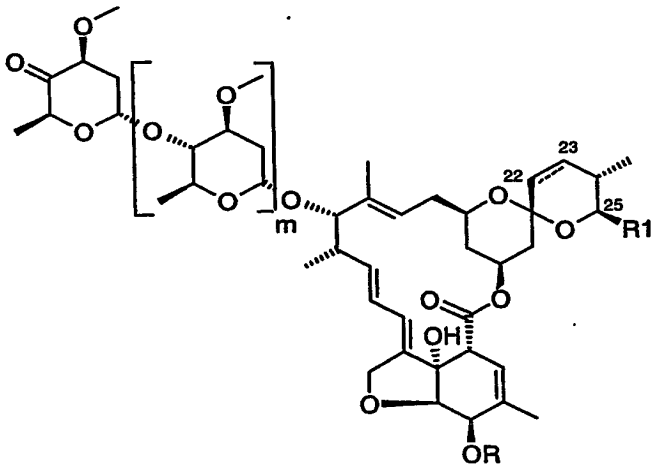


(IId),

wherein Q has the meaning as defined above in formula (II).

The invention further provides a process for preparing the compounds of the formula (I) and, if appropriate, tautomers thereof, wherein R_1 to R_6 have the same meanings as given above under (1) for formula (I), and m is 0 or 1, n is 0 and p is 0 or 1, characterized in that

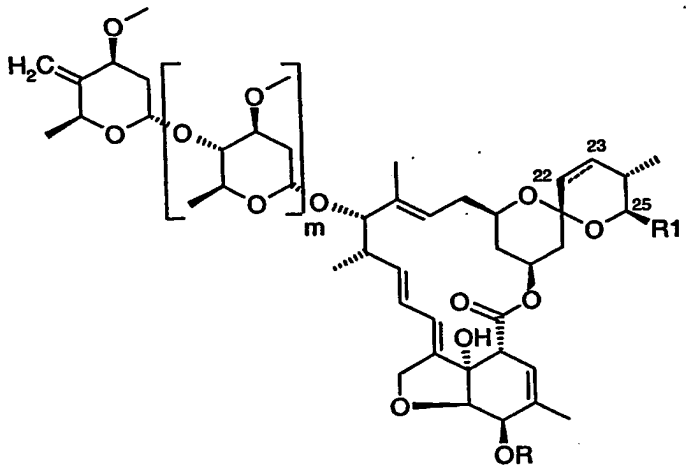
(F) a compound of the above formula (II) is oxidized to a compound of the formula



(IV),

which are partly known or can be prepared according to methods known per se, and wherein R_1 and m are as defined for formula (I) and R is a protecting group,

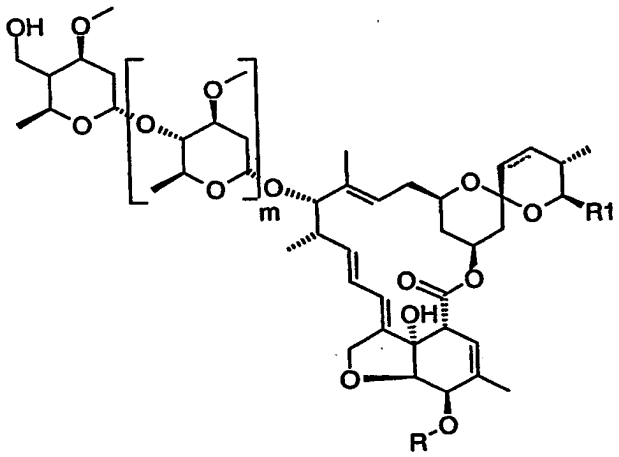
(G) converting the above compound of the formula (IV) into a compound of the formula



(V),

which are partly known or can be prepared according to methods known per se, wherein m and R_1 have the meanings as defined above and R is a protecting group, and which is known;

(H) further converting the compound of the formula (V) preferably via hydroboration and oxidative work-up into a compound of the formula

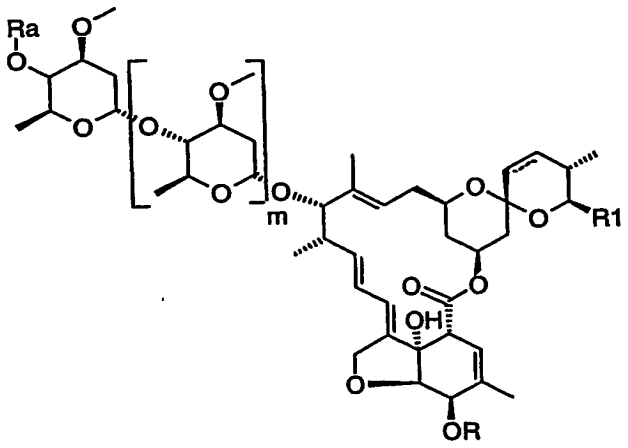


(VI),

wherein m and R_1 have the meanings as defined above for formula (I).

The invention further provides a process for preparing the compounds of the formula (I) and, if appropriate, tautomers thereof, wherein R_1 to R_6 have the same meanings as given above under (1) for formula (I), and m is 0 or 1, n is 0 and p 0 or 1, characterized in that

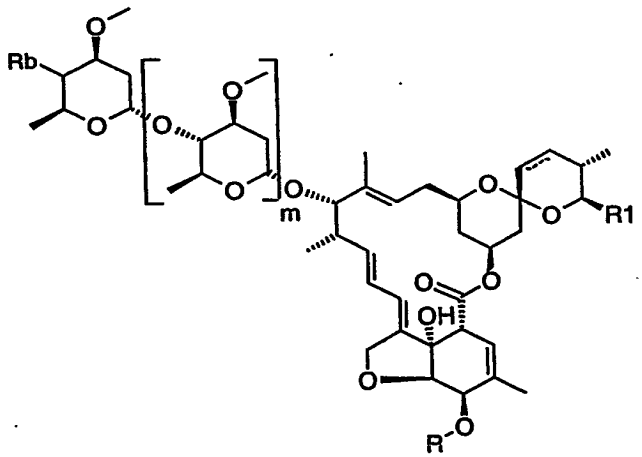
(J) a compound of the formula (II) as defined above is converted into a compound of the formula



(VII),

wherein m and R_1 have the meanings as defined above, R is a protecting group and R_a is an activating group such as an optionally substituted alkyl- or arylsulphonate;

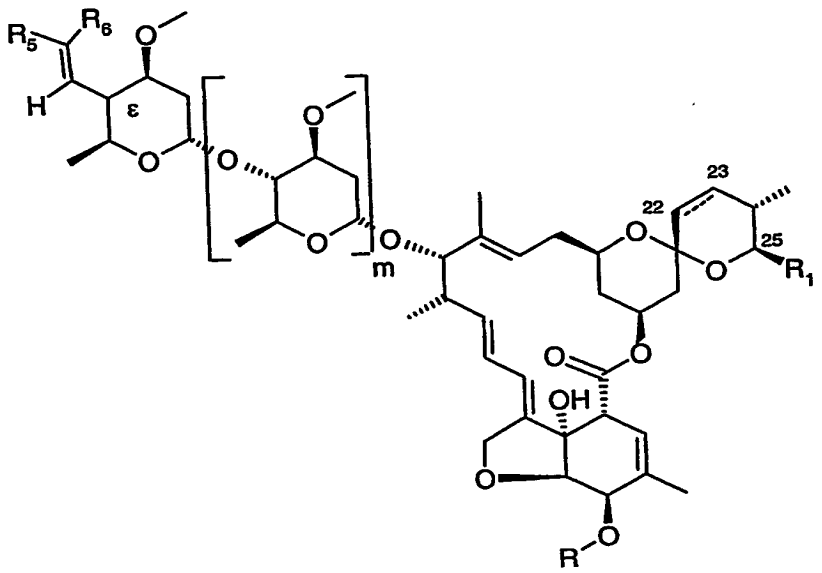
(K) further converting the said compound of the formula (VII) into a compound of the formula



(VIII),

wherein R is a protecting group, m and R_1 have the meanings as defined above for formula (VIII), and R_b is either halogen or CN; and

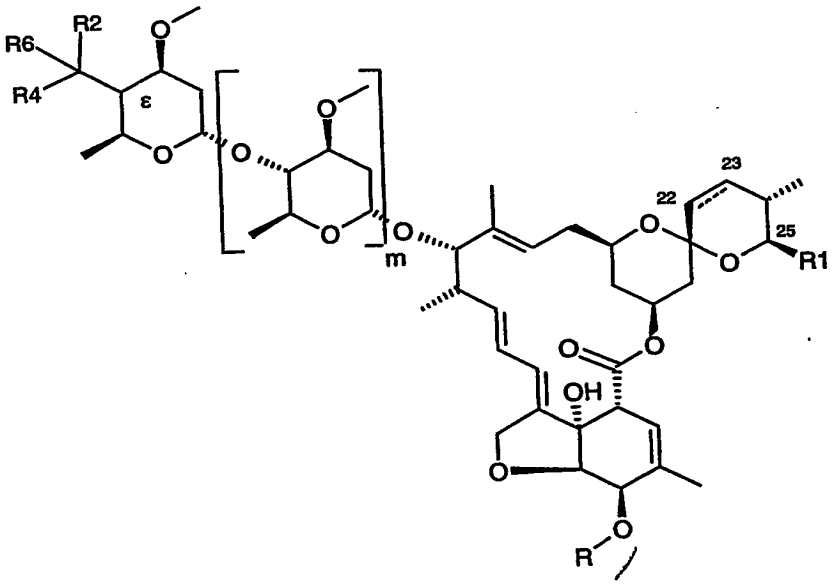
(L) further converting the compound of the formula (VIII) wherein R_b is iodine, into a compound of the formula



(IX),

wherein R, m, R_1, R_5 and R_6 have the meanings as defined above for formula (I); or into a compound of formula (IIa) as defined before; or

(M) converting the compound of the formula (VIII) wherein R_b is iodine, into acompound of the formula



(X),

wherein R, m, R_1, R_2, R_4 and R_6 have the meanings as defined above for formula (I);

(N) Compounds of formula (I) can be obtained from compounds of formulae (IIa), (IIb), (IIc), (IId), (VI), (VIII), (IX) and (X) as defined above by removing the protecting group at the 5-position of the forementioned intermediates.

The compounds of the formulae (I) and (II) can further be converted into other compounds of the formula (I) by methods known per se, for instance for preparing a compound of the formula (I), wherein R_2 and R_3 are a bond, by reacting compounds of the formulae (IIb) or (IId) with a compound of the formula R_5-CH_2-R_6, wherein R_5 and R_6 have the meaning as defined under (1); or by reacting a compound of the formulae (IIa), (V) or (XI) with a compound of the formula $R_5R_6C{=}CH_2$.

Furthermore compounds of formula (IIa), (IIb), (IIc), (IId), (VI), (VIII), (IX) and (X) bearing a functional group in its free or protected form can be used as starting materials for the preparation of further compounds of formula (I). For example, a compound of formula (IId) can be converted by deprotection into a compound of formula (I) wherein n = 1, R_2 and R_4 together are oxygen, p = 0 and R_6 is OH.

Furthermore compounds of formula (IIa), (IIb), (IIc), (IId), (VI), (VIII), (IX) and (X) bearing a substituent at the ε-position (4'- or 4"-position) in its free or protected form can be used as starting materials for the preparation of further compounds of formula (I). For example, a compound of formula (IId) can be converted by deprotection into a compound of formula (I) wherein n = 1, R_2 and R_4 together are oxygen, p = 0 and R_6 is OH.

The compound of the formula (VI) can further be derivatized by known procedures, for case by reacting the compound with a compound Hal-C(=X)-R_7, wherein R_7 is as defined under (1) and Hal is a halogen.

The comments made above in connection with tautomers of compounds of formula (I) apply analogously to the starting materials mentioned hereinabove and hereinbelow in respect of their tautomers and diasteromers.

The reactions described hereinabove and hereinbelow are carried out in a manner known *per se*, for example in the absence or, customarily, in the presence of a suitable solvent or diluent or of a mixture thereof, the reactions being carried out, as required, with cooling, at room temperature or with heating, for example in a temperature range of approximately from -80°C to the boiling temperature of the reaction medium, preferably from approximately 0°C to approximately +150°C, and, if necessary, in a closed vessel, under pressure, under an inert gas atmosphere and/or under anhydrous conditions. Especially advantageous reaction conditions can be found in the Examples.

The reaction time is not critical; a reaction time of from about 0.1 to about 24 hours, especially from about 0.5 to about 10 hours, is preferred.

The product is isolated by customary methods, for example by means of filtration, crystallisation, distillation or chromatography, or any suitable combination of such methods.

Protecting groups are as defined for instance in the compounds of formulae (II), (IV), (V), (VII) and (VIII) include: alkyl ether radicals, such as methoxymethyl, methylthiomethyl, tert-butylthiomethyl, benzyloxymethyl, p-methoxybenzyl, 2-methoxyethoxymethyl, 2,2,2-trichloroethoxymethyl, 2-(trimethylsilyl)ethoxymethyl, tetrahydropyranyl, tetrahydrofuranyl, 1-ethoxyethyl, 1-(2-chloroethoxy)ethyl, 1-methyl-1-methoxyethyl, 1-methyl-1-benzyloxyethyl, trichloroethyl, 2-trimethylsilylethyl, tert-butyl, allyl, p-methoxyphenyl, 2,4-dinitrophenyl, benzyl, p-methoxybenzyl, o-nitrobenzyl, p-nitrobenzyl, triphenylmethyl; trialkylsilyl radicals, such as trimethylsilyl, triethylsilyl, dimethyl-tert-butylsilyl, dimethyl-isopropylsilyl, dimethyl-1,1,2-trimethylpropylsilyl, diethyl-isopropylsilyl, dimethyl-tert-hexylsilyl, but also phenyl-tert-alkylsilyl groups, such as diphenyl-tert-butylsilyl; esters, such as formates, acetates, chloroacetates, dichloroacetates, trichloroacetates, trifluoroacetates, methoxyacetates, phenoxyacetates, pivaloates, benzoates; alkyl carbonates, such as methyl-, 9-fluorenylmethyl-, ethyl-, 2,2,2-trichloroethyl-, 2-(trimethylsilyl)ethyl-, vinyl-, allyl-, benzyl-, p-methoxybenzyl-, o-nitrobenzyl-, p-nitrobenzyl-, but also p-nitrophenyl-carbonate.

Preference is given to trialkylsilyl radicals, such as trimethylsilyl, triethylsilyl, dimethyl-tert-butylsilyl, diphenyl-tert-butylsilyl, esters, such as methoxyacetates and phenoxyacetates, and carbonates, such as 9-fluorenylmethylcarbonates and allylcarbonates. Dimethyl-tert-butylsilyl ether is especially preferred.

The starting materials mentioned hereinabove and hereinbelow that are used for the preparation of the compounds of formula (I) and, where applicable, their tautomers are known or can be prepared by methods known *per se*, e.g. as indicated below.

The compounds of formulae (II), (III), (IV), (V), (VI), (VII) and (VIII) are partly new, in which case they are also an aspect of the invention. They are valuable intermediates for the synthesis of compounds of formula (I), and can prepared by methods known *per se*. The use of compounds of formula (II) and of formula (III) for the synthesis of compounds of formula (I) are also a subject of this invention. The preferences for the substituents are the same as defined for the compound of the formula (I) in (2) to (20).

Process variant (A):

Examples of solvents and diluents include: aromatic, aliphatic and alicyclic hydrocarbons and halogenated hydrocarbons, such as benzene, toluene, xylene, mesitylene,

tetralin, chlorobenzene, dichlorobenzene, bromobenzene, petroleum ether, hexane, cyclohexane, dichloromethane, trichloromethane, tetrachloromethane, dichloroethane, trichloroethene or tetrachloroethene; ethers, such as diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, tert-butyl methyl ether, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol dimethyl ether, dimethoxydiethyl ether, tetrahydrofuran or dioxane; esters of carboxylic acids, such as ethyl acetate; amides, such as dimethylformamide, dimethylacetamide or 1-methyl-2-pyrrolidinones; nitriles, such as acetonitrile; sulfoxides, such as dimethyl sulfoxide; or mixtures of the mentioned solvents. Preference is given to amides, such as dimethylformamide and dimethylacetamide, especially dimethylacetamide, halogenated hydrocarbons, such as dichloromethane and aromatic hydrocarbons such as toluene.

The reactions are advantageously carried out in a temperature range of from approximately -70°C to +80°C, preferably at from 0°C to +60°C.

Examples of thiocarbonylating agents are known to a person skilled in the art; they include 1,1'-thiocarbonyldiimidazole and arylchlorothionoformates; especially suitable are 1,1'-thiocarbonyldiimidazole and *p*-tolyl chlorothionoformate.

In a preferred embodiment of Variant (A) the reaction is carried out with *p*-tolyl chlorothionoformate in the presence, or absence, of 4-(dimethylamino)pyridine at room temperature in dichloromethane or with 1,1'-thiocarbonyldiimidazole at 20-60°C in N,N-dimethylformamide.

Especially preferred conditions for the reaction are described in Examples P1 (Step A) and P13 (Step A).

Process variant (B):

Examples of solvents and diluents include: aromatic, aliphatic and alicyclic hydrocarbons and halogenated hydrocarbons, such as benzene, toluene, xylene, mesitylene, tetralin, chlorobenzene, dichlorobenzene, petroleum ether, hexane, and cyclohexane; alcohols such as diisopropyl alcohol and *tert*-butanol; or mixtures of the mentioned solvents. Preference is given to aromatic hydrocarbons, such as benzene, and toluene.

The reactions are advantageously carried out in a temperature range from approximately -70°C to to the boiling point of the solvent used, preferably from +60°C to +120°C.

Examples of allylating agents are known to a person skilled in the art; they include optionally substituted allylic stannanes, for example, allyl-tri-*n*-butyltin, and sulphones. Especially suitable substituted allylic stannanes are stannanes with carboxyalkyl, alkyl, tri-alkylsilyl, tri-arylsilyl, CH_2(tri-alkylsilyl) and CH_2(tri-arylsilyl) substitutents at C2.

The reaction is carried out in the presence of radical initiators known to a person skilled in the art; they include 1,1'-azobis(cyclohexanecarbonitrile) and 2,2'-azobis-(2-methyl-butyronitrile).

In a preferred embodiment of Variant (B) the allylation reaction is carried out in the presence of 1,1'-azobis(cyclohexanecarbonitrile) at +60 to +110 °C in chlorobenzene as the solvent.

Especially preferred conditions for the reaction are described in Examples P1 (Step B) and P13 (Step B).

Process variant (C):

Examples of solvents and diluents include: aromatic, aliphatic and alicyclic hydrocarbons and hydrocarbons, such as benzene, toluene, xylene, mesitylene, Tetralin; alcohols, such as methanol, ethanol, propanol, isopropanol, butanol, ethylene glycol or glycerol; amides, such as N,N-dimethylformamide, N,N-diethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone or hexamethylphosphoric acid triamide; nitriles, such as acetonitrile or propionitrile; and sulfoxides, such as dimethyl sulfoxide; and also water; or mixtures of the mentioned solvents; especially suitable are amides, alcohols, water, or mixtures thereof, more especially N,N-dimethylformamide, N,N-dimethylacetamide or water.

The reactions are advantageously carried out in a temperature range from room temperature to +60°C; preferance being given to reaction from +10 to +30°C.

In a preferred embodiment of Variant (C) the oxidation is carried out in the presence of palladium dichloride, copper (II) acetate and oxygen room temperature in N,N-dimethyl-acetamide and water as the solvent.

Especially preferred conditions for the reaction are described in Examples P8 and P14 (Step A).

Process variant (D):

Examples of solvents and diluents include: aromatic, aliphatic and alicyclic hydrocarbons and halogenated hydrocarbons, such as benzene, toluene, xylene, mesitylene,

Tetralin, chlorobenzene, dichlorobenzene, bromobenzene, petroleum ether, hexane, cyclohexane, dichloromethane, tetrachloromethane, dichloroethane, trichloroethene or tetrachloroethene; ethers, such as diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, tert-butyl methyl ether, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol dimethyl ether, dimethoxydiethyl ether, tetrahydrofuran or dioxane; or mixtures of the mentioned solvents; especially suitable are tetrahydrofuran, diethyl ether or dichlormethane; or the use of no solvent.

The hydroboration may be carried out in the presence, or absence, of transition-metal catalysts. Hydroborating agents include boron hydride reagents; especially suitable are borane-methyl sulphide complex, borane-tetrahydrofuran complex, dicyclohexylborane, 9-borabicyclo[3.3.1]nonane and sodium malonyloxyborohydride.

In a preferred embodiment of Variant D, the hydroboration is carried out with 9-borabicyclo[3.3.1]nonane or borane-tetrahydrofuran complex at room temperature, in tetrahydrofuran.

The alcohol products are obtained by standard oxidation of the organoboranes. Examples of standard oxidizing regents are known to a person skilled in the art; they include base/hydrogen peroxide mixtures and sodium perborate.

The reactions are advantageously carried out in a temperature range from 0 to +60°C; preferance being given to reaction from 10 to 30°C.

Especially preferred conditions for the reaction are described in Example P5 (Step A).

Process variant (E):

Examples of solvents and diluents include: aromatic, aliphatic and alicyclic hydrocarbons and halogenated hydrocarbons, such as benzene, toluene, xylene, mesitylene, Tetralin, chlorobenzene, dichlorobenzene, bromobenzene, petroleum ether, hexane, cyclohexane, dichloromethane, trichloromethane, tetrachloromethane, dichloroethane, trichloroethene or tetrachloroethene; ethers, such as diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, tert-butyl methyl ether, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol dimethyl ether, dimethoxydiethyl ether, tetrahydrofuran or dioxane; alcohols, such as methanol, ethanol, propanol, isopropanol, butanol, ethylene glycol or glycerol; nitriles, such as acetonitrile or propionitrile; ketones, such as acetone and also water; or mixtures of the mentioned solvents; especially suitable are

ethers, alcohols, water, or mixtures thereof, more especially tetrahydrofuran, *tert*-butanol or water.

Examples of agents for oxidatively cleaving the terminal alkene function are known to a person skilled in the art; they include for example reagent combinations of OsO_4, N-methyl-morpholine-N-oxide and sodium periodate.

The reactions are advantageously carried out in a temperature range from room temperature to +60°C; preferance being given to reaction from +10 to +30°C.

Especially preferred conditions for the reaction are described in Example P3 (Step A).

Process variant (F):

Examples of solvents include those listed above under process variant (A).

The reactions are advantageously carried out in a temperature range from approximately -70°C to +80°C.

Examples of oxidising agents are known to a person skilled in the art, for instance using oxalyl chloride or trifluoroacetic anhydride and dimethylsulfoxide or 1,1,1-tris(acetyloxy)-1,1-dihydro-1,2-benziodoxol-3-(1H)-one.

Process variant (G):

Examples of solvents include those listed above under process variant (A), especially suitable are aromatic, aliphatic and alicyclic hydrocarbons, ethers, and sulphoxides or mixtures thereof, more especially toluene, tetrahydrofuran, diethyl ether and dimethyl sulphoxide.

The reactions are advantageously carried out in a temperature range from approximately -78°C to +80°C, preferably from –40 to +60 °C.

Examples of methylenating agents are known to a person skilled in the art, for instance dimethyl titanocene or a reagent prepared from Zn, dihalomethane and $TiCl_4$, or methylene triphenylphosphorane.

In a preferred embodiment of Variant (G) the reaction is carried out in the presence of zinc, diiodomethane and a Lewis acid, such as titanium tetrachloride, in dichloromethane and tetrahydrofuran as the solvent at 0 to +30 °C.

Especially preferred conditions for this process are described, for example, in Example P.10 (step A).

Process variant (H):

Examples of solvents and diluents include: aromatic, aliphatic and alicyclic hydrocarbons and halogenated hydrocarbons, such as benzene, toluene, xylene, mesitylene, Tetralin, chlorobenzene, dichlorobenzene, bromobenzene, petroleum ether, hexane, cyclohexane, dichloromethane, tetrachloromethane, dichloroethane, trichloroethene or tetrachloroethene; ethers, such as diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, tert-butyl methyl ether, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol dimethyl ether, dimethoxydiethyl ether, tetrahydrofuran or dioxane; or mixtures of the mentioned solvents; especially suitable are tetrahydrofuran, diethyl ether or dichlormethane; or the use of no solvent.

Examples of hydroboration-oxidation agents are known to a person skilled in the art. The hydroboration may be carried out in the presence, or absence, of transition-metal catalysts as known to those persons skilled in the art. Hydroborating agents include boron hydride reagents; especially suitable are borane-methyl sulphide complex and borane-tetrahydrofuran complex.

In a preferred embodiment of variant (H), the hydroboration is carried out with borane-tetrahydrofuran complex at room temperature, in tetrahydrofuran as the solvent.

The alcohol products are obtained by standard oxidation of the organoboranes. Examples of standard oxidizing reagents are known to a person skilled in the art; they include base/hydrogen peroxide mixtures and sodium perborate.

The reactions are advantageously carried out in a temperature range from 0 to +60°C; preference being given to reaction from +10 to +30°C.

Especially preferred conditions for the reaction are described in Example P.10 (step B).

Process variant (J):

Examples of solvents and diluents include those listed above under Process variant (A); especially suitable are halogenated hydrocarbons, for example, dichloromethane.

The reactions are advantageously carried out in a temperature range of from about -30 to +50°C; preference being given to reaction at -10°C to +30°C.

In a preferred embodiment of Variant (D) the reaction is carried out with trifluoromethanesulphonyl chloride in the presence of an organic base, such as triethyl amine or N,N-diisopropylethylamine and 4-(dimethylaminopyridine at 0 to +20°C in dichloromethane as the solvent.

Especially preferred conditions for this Process variant are described, for example, in Example P.2 (step A).

Process variant (K):

Examples of solvents and diluents include those listed above under Process variant (A); especially suitable are amides, for example N,N-dimethylformamide.

The reactions are advantageously carried out in a temperature range of from about -10 °C to the boiling point of the solvent used; preference being given to reaction at 0°C to +30°C.

In a preferred embodiment of Variant (K) the reaction is carried out with tetra *n*-butyl ammonium cyanide, potassium iodide or sodium dimethylmalonate at 0 to +30°C in N,N-dimethylformamide as the solvent.

Especially preferred conditions for this Process variant are described, for example, in Example P.11 (step A).

Process variant (L):

Examples of solvents and diluents include those listed above under Process variant (A); especially suitable are aromatic hydrocarbons and halogenated aromatic hydrocarbons, for example, chlorobenzene.

The reactions are advantageously carried out in a temperature range of from about room temperature to the boiling point of the solvent used; preference being given to reaction at +60°C to +110°C.

Examples of vinylating agents are known to a person skilled in the art; they include optionally substituted vinylic stannanes and vinylic sulphones, for example, tri-*n*-butyl-((*E/Z*)-styryl)-stannane or 2,2-dichlorovinyl ethyl sulphone.

The reaction is carried out in the presence of radical initiators known to a person skilled in the art; they include 1,1'-azobis(cyclohexanecarbonitrile), 2,2'-azobis-(2-methylbutyronitrile) and di-*tert*-butylperoxide.

In a preferred embodiment of Variant (L) the vinylation reaction is carried out in the presence of 1,1'-azobis(cyclohexanecarbonitrile) at +60 to +110°C in chlorobenzene as the solvent.

Especially preferred conditions for this Process variant are described, for example, in Example P.2 (step C).

Process variant (M):

Examples of solvents and diluents include those listed above under Process variant (A); especially suitable are amides, for example N,N-dimethylformamide.

The reactions are advantageously carried out in a temperature range of from about 0°C to the boiling point of the solvent used; preference being given to reaction at 0°C to +40°C.

Examples of alkylating agents are known to a person skilled in the art; they include optionally substituted activated methylene compounds, for example, malononitrile, ethylcyanoacetate and malonic acid dimethyl ester.

In a preferred embodiment of Variant (M) the reaction is carried out at 0 to +30°C in N,N-dimethylformamide as the solvent.

Especially preferred conditions for this Process variant are described, for example, in Example P.12 (step A).

Process variant (N):

Examples of solvents and diluents are the same as those mentioned under Process variant A. In addition, alcohols, such as methanol, ethanol or 2-propanol, and water are suitable.

The reactions are advantageously carried out in a temperature range of approximately from -70°C to 100°C, preferably at from -10°C to 25°C.

There are suitable for the removal of the protecting group Lewis acids, such as hydrochloric acid, methanesulfonic acid, HF in pyridine, p-toluenesulfonic acid; ammonium fluoride, such as tetrabutylammonium fluoride; bases, such as ammonia, trialkylamine or heterocyclic bases; hydrogenolysis with a catalyst, such as palladium-on-carbon; reducing agents, such as sodium borohydride or tributyltin hydride with a catalyst, such as $Pd(PPh_3)_4$, or also zinc with acetic acid.

Preference is given to acids, such as methanesulfonic acid or HF in pyridine; sodium borohydride with Pd(0); bases, such as ammonia, triethylamine or pyridine; especially acids, such as HF in pyridine or methanesulfonic acid.

Especially preferred conditions for the reaction are described in Examples P1 (Step C), P2 (Step D), P3 (Step B), P4 (Step B), P5 (Step B), P7 (Step B), P10 (Step C), P11 (Step B), P12 (Step B), P13 (Step C) and P14 (Step 2).

The compounds of formula (I) may be in the form of one of the possible isomers or in the form of a mixture thereof, in the form of pure isomers or in the form of an isomeric mixture, i.e. in the form of a diastereomeric mixture; the invention relates both to the pure isomers and to the diastereomeric mixtures and is to be interpreted accordingly hereinabove and hereinbelow, even if stereochemical details are not mentioned specifically in every case.

The diastereomeric mixtures can be resolved into the pure isomers by known methods, for example by recrystallisation from a solvent, by chromatography, for example high pressure liquid chromatography (HPLC) on acetylcellulose, with the aid of suitable micro-organisms, by cleavage with specific, immobilised enzymes, or *via* the formation of inclusion compounds, for example using crown ethers, only one isomer being complexed.

Apart from by separation of corresponding mixtures of isomers, pure diastereoisomers can be obtained according to the invention also by generally known methods of stereoselective synthesis, for example by carrying out the process according to the invention using starting materials having correspondingly suitable stereochemistry.

In each case it may be advantageous to isolate or synthesise the biologically more active isomer, where the individual components have different biological activity.

The compounds of formula (I) may also be obtained in the form of their hydrates and/or may include other solvents, for example solvents which may have been used for the crystallisation of compounds in solid form.

The invention relates to all those embodiments of the process according to which a compound obtainable as starting material or intermediate at any stage of the process is used as starting material and some or all of the remaining steps are carried out or a starting material is used in the form of a derivative or salt and/or its racemates or antipodes or, especially, is formed under the reaction conditions.

In the processes of the present invention it is preferable to use those starting materials and intermediates which result in the compounds of formula (I) that are especially preferred.

The invention relates especially to the preparation processes described in Examples 1.1 to 8.40.

In the area of pest control, the compounds of formula (I) according to the invention are active ingredients exhibiting valuable preventive and/or curative activity with a very advantageous biocidal spectrum and a very broad spectrum, even at low rates of concentration, while being well tolerated by warm-blooded animals, fish and plants. They are, surprisingly, equally suitable for controlling both plant pests and ecto- and endo-parasites in humans and more especially in productive livestock, domestic animals and pets. They are effective against all or individual development stages of normally sensitive animal pests, but also of resistant animal pests, such as insects, preferably of the orders Lepidoptera; Coleoptera, Homoptera, Orthoptera, Isoptera, Psocoptera, Anoplura, Mallophaga, Thysanoptera; Heteroptera, Siphonaptera, Hymentoptera and Thysanura, and representatives of the order Acarina, nematodes, cestodes and trematodes, while at the same time protecting useful organisms. The said animal pests especially include, for example, those mentioned in European Patent Application EP-A-736 252, page 5, line 55, to page 6, line 55. The pests mentioned therein are therefore included by reference in the subject matter of the present invention.

The insecticidal or acaricidal activity of the active ingredients according to the invention may manifest itself directly, i.e. in the mortality of the pests, which occurs immediately or only after some time, for example during moulting, or indirectly, for example in reduced oviposition and/or hatching rate, good activity corresponding to a mortality of at least 50 to 60 %.

It is also possible to control pests of the class Nematoda using the compounds according to the invention. Such pests include, for example, root knot nematodes, cyst-forming nematodes and also stem and leaf nematodes;

especially of Heterodera spp., e.g. Heterodera schachtii, Heterodora avenae and Heterodora trifolii; Globodera spp., e.g. Globodera rostochiensis; Meloidogyne spp., e.g. Meloidogyne incognita and Meloidogyne javanica; Radopholus spp., e.g. Radopholus simiis; Pratylenchus, e.g. Pratylenchus neglectans and Pratylenchus penetrans; Tylenchulus, e.g. Tylenchulus semipenetrans; Longidorus, Trichodorus, Xiphinema, Ditylenchus, Apheenchoides and Anguina; insbesondere Meloidogyne, e.g. Meloidogyne incognita, and Heterodera, e.g. Heterodera glycines.

An especially important aspect of the present invention is the use of the compounds of formula (I) according to the invention in the protection of plants against parasitic feeding pests.

The compounds according to the invention can be used to control, i.e. to inhibit or destroy, pests of the mentioned type occurring on plants, especially on useful plants and ornamentals in agriculture, in horticulture and in forestry, or on parts of such plants, such as the fruits, blossoms, leaves, stems, tubers or roots, while in some cases plant parts that grow later are still protected against those pests.

Target crops include especially cereals, such as wheat, barley, rye, oats, rice, maize and sorghum; beet, such as sugar beet and fodder beet; fruit, e.g. pomes, stone fruit and soft fruit, such as apples, pears, plums, peaches, almonds, cherries and berries, e.g. strawberries, raspberries and blackberries; leguminous plants, such as beans, lentils, peas and soybeans; oil plants, such as rape, mustard, poppy, olives, sunflowers, coconut, castor oil, cocoa and groundnuts; cucurbitaceae, such as marrows, cucumbers and melons; fibre plants, such as cotton, flax, hemp and jute; citrus fruits, such as oranges, lemons, grapefruit and mandarins; vegetables, such as spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes and paprika; lauraceae, such as avocado, cinnamon and camphor; and tobacco, nuts, coffee, aubergines, sugar cane, tea, pepper, vines, hops, bananas, natural rubber plants and ornamentals.

Further areas of use of the compounds according to the invention are the protection of stored goods and storerooms and the protection of raw materials, and also in the hygiene sector, especially the protection of domestic animals and productive livestock against pests of the mentioned type, more especially the protection of domestic animals, especially cats and dogs, from attack by fleas, ticks and nematodes.

The invention therefore relates also to pesticidal compositions, such as emulsifiable concentrates, suspension concentrates, directly sprayable or dilutable solutions, spreadable pastes, dilute emulsions, wettable powders, soluble powders, dispersible powders, wettable powders, dusts, granules and encapsulations of polymer substances, that comprise at least one of the compounds according to the invention, the choice of formulation being made in accordance with the intended objectives and the prevailing circumstances.

The active ingredient is used in those compositions in pure form, a solid active ingredient, for example, in a specific particle size, or preferably together with at least one of the adjuvants customary in formulation technology, such as extenders, e.g. solvents or solid

carriers, or surface-active compounds (surfactants). In the area of parasite control in humans, domestic animals, productive livestock and pets it will be self-evident that only physiologically tolerable additives are used.

As formulation adjuvants there are used, for example, solid carriers, solvents, stabilisers, "slow release" adjuvants, colourings and optionally surface-active substances (surfactants). Suitable carriers and adjuvants include all substances customarily used. As adjuvants, such as solvents, solid carriers, surface-active compounds, non-ionic surfactants, cationic surfactants, anionic surfactants and further adjuvants in the compositions used according to the invention, there come into consideration, for example, those described in EP-A-736 252, page 7, line 51 to page 8, line 39.

The compositions for use in crop protection and in humans, domestic animals and productive livestock generally comprise from 0.1 to 99 %, especially from 0.1 to 95 %, of active ingredient and from 1 to 99.9 %, especially from 5 to 99.9 %, of at least one solid or liquid adjuvant, the composition generally including from 0 to 25 %, especially from 0.1 to 20 %, of surfactants (% = % by weight in each case). Whereas commercial products will preferably be formulated as concentrates, the end user will normally employ dilute formulations having considerably lower concentrations of active ingredient.

The action of the compounds according to the invention and the compositions comprising them against animal pests can be significantly broadened and adapted to the given circumstances by the addition of other insecticides, acaricides or nematicides. Suitable additives include, for example, representatives of the following classes of active ingredient: organophosphorus compounds, nitrophenols and derivatives, formamidines, ureas, carbamates, pyrethroids, chlorinated hydrocarbons and Bacillus thuringiensis preparations.

Examples of especially suitable mixing partners include: azamethiphos; chlorfenvinphos; bupirimate; cypermethrin, cypermethrin high-cis; cyromazine; diafenthiuron; diazinon; dichlorvos; dicrotophos; dicyclanil; fenoxycarb; fluazuron; furathiocarb; isazofos; iodfenphos; kinoprene; lufenuron; methacriphos; methidathion; monocrotophos; phosphamidon; profenofos; diofenolan; a substance obtainable from the Bacillus thuringiensis strain GC91 or from NCTC11821; pymetrozine; bromopropylate; methoprène; disulfoton; quinalphos; taufluvalinate; thiocyclam; thiometon; aldicarb; azinphos-methyl; benfuracarb; bifenthrin; buprofezin; carbofuran; dibutylaminothio; cartap; chlorfluazuron; chlorpyrifos; cyfluthrin; alpha-cypermethrin; zeta-cypermethrin; deltamethrin; diflubenzuron; endosulfan; ethiofencarb; fenitrothion; fenazaquin; fenobucarb; fenvalerate; formothion; methiocarb; hep-

tenophos; imidacloprid; isoprocarb; methamidophos; methomyl; mevinphos; parathion; parathion-methyl; phosalone; pirimicarb; propoxur; teflubenzuron; terbufos; triazamate; abamectin; fenobucarb; tebufenozide; fipronil; beta-cyfluthrin; silafluofen; fenpyroximate; pyridaben; primicarb; pyriproxyfen; pyrimidifen; nematorin; nitenpyram; NI-25, acetamiprid; avermectin B_1 (abamectin); an insect-active extract from a plant; a preparation comprising insect-active nematodes; a preparation obtainable from Bacillus subtilis; a preparation comprising insect-active fungi; a preparation comprising insect-active viruses; AC 303 630; acephate; acrinathrin; alanycarb; alphamethrin; amitraz; AZ 60541; azinphos A; azinphos M; azocyclotin; bendiocarb; bensultap; betacyfluthrin; BPMC; brofenprox; bromophos A; bufencarb; butocarboxim; butylpyridaben; cadusafos; carbaryl; carbophenothion; chloethocarb; chlorethoxyfos; chlormephos; cis-res-methrin; clocythrin; clofentezine; cyanophos; cycloprothrin; cyhexatin; demeton M; demeton S; demeton-S-methyl; dichlofenthion; dicliphos; diethion; dimethoate; dimethylvinphos; dioxathion; edifenphos; emamectin; esfenvalerate; ethion; ethofenprox; ethoprophos; etrimphos; fenamiphos; fenbutatin oxide; fenothiocarb; fenpropathrin; fenpyrad; fenthion; fluazinam; flucycloxuron; flucythrinate; flufenoxuron; flufenprox; fonophos; fosthiazate; fubfenprox; HCH; hexaflumuron; hexythiazox; IKI-220; iprobenfos; isofenphos; isoxathion; ivermectin; lambda-cyhalothrin; malathion; mecarbam; mesulfenphos; metaldehyd; metolcarb; milbemectin; moxidectin; naled; NC 184; omethoate; oxamyl; oxydemethon M; oxydeprofos; permethrin; phenthoate; phorate; phosmet; phoxim; pirimiphos M; pirimiphos A; promecarb; propaphos; prothiofos; prothoate; pyrachlophos; pyrada-phenthion; pyresmethrin; pyrethrum; RH 5992; salithion; sebufos; sulfotep; sulprofos; tebufenpyrad; tebupirimphos; tefluthrin; temephos; terbam; tetrachlorvinphos; thiacloprid; thiamethoxam; thiafenox; thiodicarb; thiofanox; thionazin; thuringiensin; tralomethrin; triarathen; triazophos; triazuron; trichlorfon; triflumuron; trimethacarb; vamidothion; xylylcarb; YI 5301/5302; zetamethrin; DPX-MP062; RH-2485; D 2341 or XMC (3,5-xylyl methylcarbamate).

Preferred crop protection products have especially the following compositions (% = percent by weight):

Emulsifiable concentrates:

active ingredient:	1 to 90%, preferably 5 to 20%
surfactant:	1 to 30%, preferably 10 to 20%
solvent:	5 to 98%, preferably 70 to 85%

Dusts:

active ingredient:	0.1 to 10%, preferably 0.1 to 1%
solid carrier:	99.9 to 90%, preferably 99.9 to 99%

Suspension concentrates:

active ingredient:	5 to 75%, preferably 10 to 50%
water:	94 to 24%, preferably 88 to 30%
surfactant:	1 to 40%, preferably 2 to 30%

Wettable powders:

active ingredient:	0.5 to 90%, preferably 1 to 80%
surfactant:	0.5 to 20%, preferably 1 to 15%
solid carrier:	5 to 99%, preferably 15 to 98%

Granules:

active ingredient:	0.5 to 30%, preferably 3 to 15%
solid carrier:	99.5 to 70%, preferably 97 to 85%

The compositions according to the invention may also comprise further solid or liquid adjuvants, such as stabilisers, e.g. vegetable oils or epoxidised vegetable oils (e.g. epoxidised coconut oil, rapeseed oil or soybean oil), antifoams, e.g. silicone oil, preservatives, viscosity regulators, binders and/or tackifiers as well as fertilisers or other active ingredients for obtaining special effects, e.g. acaricides, bactericides, fungicides, nematicides, molluscicides or selective herbicides.

The crop protection products according to the invention are prepared in known manner, in the absence of adjuvants, e.g. by grinding, sieving and/or compressing a solid active ingredient or mixture of active ingredients, for example to a certain particle size, and in the presence of at least one adjuvant, for example by intimately mixing and/or grinding the active ingredient or mixture of active ingredients with the adjuvant(s). The invention relates likewise to those processes for the preparation of the compositions according to the invention and to the use of the compounds of formula (I) in the preparation of those compositions.

The invention relates also to the methods of application of the crop protection products, i.e. the methods of controlling pests of the mentioned type, such as spraying,

atomising, dusting, coating, dressing, scattering or pouring, which are selected in accordance with the intended objectives and the prevailing circumstances, and to the use of the compositions for controlling pests of the mentioned type. Typical rates of concentration are from 0.1 to 1000 ppm, preferably from 0.1 to 500 ppm, of active ingredient. The rates of application per hectare are generally from 1 to 2000 g of active ingredient per hectare, especially from 10 to 1000 g/ha, preferably from 20 to 600 g/ha.

A preferred method of application in the area of crop protection is application to the foliage of the plants (foliar application), the frequency and the rate of application being dependent upon the risk of infestation by the pest in question. However, the active ingredient can also penetrate the plants through the roots (systemic action) when the locus of the plants is impregnated with a liquid formulation or when the active ingredient is incorporated in solid form into the locus of the plants, for example into the soil, e.g. in granular form (soil application). In the case of paddy rice crops, such granules may be applied in metered amounts to the flooded rice field.

The crop protection products according to the invention are also suitable for protecting plant propagation material, e.g. seed, such as fruits, tubers or grains, or plant cuttings, including propagation material of genetically modified plants, against animal pests. The propagation material can be treated with the composition before planting: seed, for example, can be dressed before being sown. The active ingredients according to the invention can also be applied to grains (coating), either by impregnating the seeds in a liquid formulation or by coating them with a solid formulation. The composition can also be applied to the planting site when the propagation material is being planted, for example to the seed furrow during sowing. The invention relates also to such methods of treating plant propagation material and to the plant propagation material so treated.

Preparation Examples:

Example P1: 4"-Deoxy-4"-(*S*)-allyl-avermectin B_1 and 4"-deoxy-4"-(*R*)-allyl-avermectin B_1

Step A: To a solution of 15 g 5-O-*tert*-butyldimethylsilyl-avermectin B_1 and 6 ml pyridine in 150 ml dichloromethane at 0°C is added 7 ml *p*-tolyl chlorothionoformate and a catalytic amount of 4-(dimethylamino)pyridine. The reaction mixture is stirred for 2 hours at room temperature, poured into water, extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated. Flash chromatography (silica gel, hexane/ethyl acetate 9/1) affords the

corresponding 4"-O-(4-methylphenoxythionocarbonyl)-5-O-*tert*-butyldimethylsilyl avermectin B_1.

Step B: A degassed solution of 1.5 g of 4"-O-(4-methylphenoxythionocarbonyl)-5-O-*tert*-butyldimethylsilyl avermectin B_1 10 ml in chlorobenzene is heated at 100°C under argon. 4 ml Allyltributyltin, then 72 mg 1,1'-azobis(cyclohexanecarbonitrile) are added and the solution is stirred at 100°C for 20 hours. The mixture is concentrated and the residue purified by flash chromatography (silica gel, hexane/ethyl acetate 9/1) providing 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-(*S*)-allyl-avermectin B_1 ~~(36%)~~ and 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-(*R*)-allyl-avermectin B_1 ~~(5%)~~ along with 5-OTBDMS-4"-deoxy-Avermectin B_1.

Step C: To a solution of 100 mg of 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-(*S*)-allyl-avermectin B_1 in 5 ml tetrahydrofuran is added 1 ml of a solution of HF-pyridine (25 g commercial 70% HF-pyridine solution, 27.5 ml tetrahydrofuran, 12.5 ml pyridine) and the mixture is stirred overnight at room temperature, poured into water, extracted with diethyl ether, washed with saturated $NaHCO_3$, brine, dried over Na_2SO_4, and concentrated. Flash chromatography (silica gel, hexane/ethyl acetate 7/3) affords 4"-deoxy-4"-(*S*)-allyl-avermectin B_1, (compound 5.1).

The corresponding 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-(*R*)-allyl-avermectin B_1 epimer provides 4"-deoxy-4"-(*R*)-allyl-avermectin B_1 in an identical manner.

4"-Deoxy-4"-(*S*)-allyl-avermectin B_1: $C_{51}H_{76}O_{13}$, MW: 896.5. LCMS: t_{RT}, B_{1a}: 11.99 min., 919.5 (M+Na); 1H NMR (500 MHz, $CDCl_3$) selected data, δH (ppm): 1.41 (m, 1H, CH-4"), 3.26 (t, *J* = 8.5 Hz, 1H, CH-4'), 3.31 (dd, *J*= 2.2, 3.8 Hz, 1H, CH-2), 3.37 (s, 3H, OCH_3), 3.44 (s, 3H, OCH_3), 3.75 (dq, *J* = 10.3, 6.2 Hz, 1H, CH-5"), 3.98 (d, 1H, *J* = 5.4 Hz, CH-6), 4.30 (m, 1H, CH-5), 5.04 (d, J = 10.2 Hz, 1H, $=CH_2$), 5.07 (d, J = 16.6 Hz, 1H, $=CH_2$), 5.81 (m, 1H, -CH=).

4"-Deoxy-4"-(*R*)-allyl-avermectin B_1: $C_{51}H_{76}O_{13}$, MW: 896.5. LCMS: t_{RT}, B_{1a}: 12.38 min., 919.5 (M+Na); 1H NMR (500 MHz, $CDCl_3$) selected data, δH (ppm): 1.96 (m, 1H, CH-4"), 3.24 (t, *J* = 8.5 Hz, 1H, CH-4'), 3.31 (dd, *J*= 2.2, 3.8 Hz, 1H, CH-2), 3.34 (s, 3H, OCH_3), 3.44 (s, 3H, OCH_3), 3.70 (dt, *J* = 12.0, 4.4 Hz, 1H, CH-3"), 3.98 (d, 1H, *J* = 5.4 Hz, CH-6), 4.30 (m, 1H, CH-5), 4.95 (d, J = 10.0 Hz, 1H, $=CH_2$), 5.07 (d, J = 16.1 Hz, 1H, $=CH_2$), 5.90 (m, 1H, -CH=).

Example P2: 4"-Deoxy-4"-(*S*)-β-Styryl-Avermectin B_1

Step A: To a solution of 5 g of 5-O-*tert*-butyldimethylsilyl-4"-*epi*-avermectin B_1 in 35 ml CH_2Cl_2 at –30°C are added 3.7 g 4-(dimethylamino)pyridine, 5.2 ml diisopropylethylamine, and finally 3.4 ml trifluoromethanesulfonic anhydride dropwise. The dark orange mixture is allowed to warm to 0°C and stirring at this temperature is continued for 3 hours. The reaction mixture is diluted with CH_2Cl_2, washed with water, dried over Na_2SO_4 and concentrated. The residue is filtered on silica gel (hexane/ethyl acetate 3/1) affording 5-O-*tert*-butyldimethylsilyl -4"-*epi*-avermectin B_1-trifluoromethanesulfonate.

Step B: 742 mg Potassium iodide are added to a solution 5 g of 5-O-*tert*-butyldimethylsilyl-4"-*epi*-avermectin B_1 trifluoromethanesulfonate in 40 ml N,N-dimethylformamide at –10°C, and the reaction mixture is stirred for 2 hours. Water is added, and the mixture is extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated. Filtration on silica gel (hexane/ethyl acetate 3/1) affords 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-(*S*)-iodo-avermectin B_1.

Step C: 2 g β-Tributylstannylstyrene and 100 mg of 1,1'-azobis(cyclohexanecarbonitrile) are added to a solution of 570 mg of 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-(*S*)-iodo-avermectin B_1 in 5 ml chlorobenzene under argon. The solution is heated at 100°C and stirred at this temperature for 8 hours. Evaporation of the solvent under reduced pressure followed by flash chromatography (silica gel, hexane/ethyl acetate 85/15) affords 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-(*S*)-β-styryl-avermectin B_1 along with 5-O-*tert*-butyldimethylsilyl-4"-deoxy-avermectin B_1.

Step D: 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-(*S*)-β-styryl-avermectin B_1 is treated as described in Example P.1, Step C to give 4"-deoxy-4"-(*S*)-β-styryl-avermectin B_1 (compound 5.5).

4"-Deoxy-4"-(*S*)-β-styryl-avermectin B_1: $C_{56}H_{78}O_{13}$, MW: 958.5. LCMS: t_{RT}, B_{1a}: 12.19 min., 981.5 (M+Na), 959.6 (M+H).

Example P3: 4"-Deoxy-Avermectin B_1-4"-(*S*)-Acetaldehyde

Step A: To a solution of 1.7 g of 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-(*S*)-allyl-avermectin B_1 (Example P1, Step B) in 25 ml tetrahydrofuran is added a solution of sodium 900 mg periodate in 25 ml water, then 1 ml OsO_4 (2.5% in tBuOH) is added; the resulting mixture is stirred for 24 hours, filtered, washed with water, brine, dried over Na_2SO_4, and concentrated. Flash chromatography (silica gel, hexane/ethyl acetate 7/3) affords 5-O-*tert*-butyldimethylsilyl-4"-deoxy-avermectin B_1-4"-(*S*)-acetaldehyde.

Step B: 5-O-*tert*-Butyldimethylsilyl-4"-deoxy-avermectin B_1-4"-(*S*)-acetaldehyde is treated as described in Example P1, Step C affording 4"-deoxy-Avermectin B_1-4"-(*S*)-acetaldehyde (compound 4.1).

4"-Deoxy-avermectin B_1-4"-(*S*)-acetaldehyde: $C_{50}H_{74}O_{14}$, MW: 898.5. LCMS: t_{RT}, B_{1a}: 9.81 min., 921.6 (M+Na), 899.5 (M+H); 1H NMR (300 MHz, $CDCl_3$) selected data, δH (ppm): 3.28 (s, 3H, OCH_3), 3.45 (s, 3H, OCH_3), 9.66 (s, 1H, CHO).

Example P4: 4"-Deoxy-4"-(*S*)-(2-Hydroxy-ethyl)-Avermectin B_1

Step A: 250 mg of 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-(*S*)-acetaldehydic-Avermectin B_1 in 10 ml methanol is reduced with 28 mg sodium borohydride at 0°C. After 30 min., the reaction mixture is poured into water, extracted with diethyl ether, dried over Na_2SO_4, and concentrated.

Step B: Crude residue of step A is treated as described in Example P.1, Step C affording 4"-deoxy-4"-(*S*)-(2-hydroxy-ethyl)-avermectin B_1 (compound 2.1).

4"-Deoxy-4"-(*S*)-(2-hydroxy-ethyl)-avermectin B_1: $C_{50}H_{76}O_{14}$, MW: 900.5. LCMS: t_{RT}, B_{1a}: 8.71 min., 923.5 (M+Na).

Example P5: 4"-Deoxy-4"-(*S*)-(3-Hydroxy-propyl)-Avermectin B_1

Step A: To a solution of 200 mg 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-(*S*)-allyl-avermectin B_1 in tetrahydrofuran (12 ml) is added 0.7 ml BH_3·tetrahydrofuran (1M in tetrahydrofuran) and the mixture is stirred at room temperature for 5 hours. The solution is cooled to 0°C, and 2,8 ml 3N sodium hydroxide is added, followed by 2.8 ml 30% aqueous hydrogen peroxide. After 1h at 0°C, the reaction mixture is poured into water, extracted with ethyl acetate, washed with water, brine, dried over Na_2SO_4, and concentrated. Flash chromatography of the residue (silica gel, hexane/ethyl acetate 65/35) affords 5-O-*tert*-butyldimethylsilyl -4"-deoxy-4"-(*S*)-(3-hydroxy-propyl)-dvermectin B_1.

Step B: 71 mg of 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-(*S*)-(3-hydroxy-propyl)-Avermectin B_1 are treated as described in Example P.1, step C, affording 4"-deoxy-4"-(*S*)-(2-hydroxy-propyl)-avermectin B_1 (compound 1.1).

4"-Deoxy-4"-(*S*)-(3-hydroxy-propyl)-avermectin B_1: $C_{51}H_{78}O_{14}$, MW: 914.5. LCMS: t_{RT}, B_{1a}: 8.64 min., 937.4 (M+Na).

Example P6: 4"-Deoxy-4"-(*S*)-(2,2-Dimethylamino-ethyl)-Avermectin B_1

To a solution of 105 mg of 4"-deoxy-avermectin B_1-4"-(*S*)-acetaldehyde in 3 ml of methanol are added 0.1 ml acetic acid, 0.08 ml dimethylamine, and finally sodium 28 mg of cyanoborohydride. The reaction mixture is stirred at room temperature for 30 min, poured into sat. $NaHCO_3$, extracted with ethyl acetate, dried over Na_2SO_4, and concentrated. 4"-deoxy-4"-(*S*)-(2,2-dimethylamino-ethyl)-avermectin B_1 is obtained, which requires no further purification (compound 2.83).

4"-Deoxy-4"-(*S*)-(2,2-dimethylamino-ethyl)-avermectin B_1: $C_{52}H_{81}NO_{13}$, MW: 927.6. LCMS: t_{RT}, B_{1a}: 5.16 min., 928.5 (M+H).

Example P7: 4"-Deoxy-4"-(*S*)-(2-Hydroxypropyl)-Avermectin B_1

Step A: A solution of 440 mg of 5-O-*tert*-butyldimethylsilyl-4"-deoxy-avermectin B_1-4"-(*S*)-acetaldehyde in 10 ml tetrahydrofuran at –10°C is treated with 0.33 ml of methylmagnesium bromide (3M in diethyl ether). The mixture is stirred at room temperature for 1 hour, quenched by the addition of sat. NH_4Cl, extracted with ethyl acetate, washed with brine, dried and concentrated. Flash chromatography (silica gel, hexane/ethyl acetate 75/25) affords the two stereoisomers of 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-(*S*)-(2-hydroxypropyl)-avermectin B_1.

Step B: Each isomer of 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-(*S*)-(2-hydroxypropyl)-avermectin B_1 is treated as described in Example P.1, step C, affording respectively the two corresponding stereoisomers of 4"-deoxy-4"-(*S*)-(2-hydroxy-propyl)-avermectin B_1 (compound 2.5).

4"-Deoxy-4"-(*S*)-(2-hydroxypropyl)-Avermectin B_1: $C_{51}H_{78}O_{14}$, MW: 914.5. LCMS: 1st isomer t_{RT}, B_{1a}: 12.36 min., 937.5 (M+Na); 2nd isomer t_{RT}, B_{1a}: 11.98 min., 937.5 (M+Na).

Example P8: 4"-Deoxy-4"-(*S*)-(2-oxo-propyl)-Avermectin B_1

A suspension of 200 mg of 4"-deoxy-4"-(*S*)-allyl-avermectin B_1 in a mixture of N,N-dimethylacetamide/water (0.45ml, 7/1) is treated with 4 mg palladium dichloride and 9 mg copper (II) acetate hydrate. The mixture is placed under oxygen at 1 atm and stirred for 24 hours. Additional $PdCl_2$ (8 mg) and $Cu(OAc)_2.H_2O$ (18mg) are added and after 48 hours the mixture is diluted with diethyl ether and filtered through celite. The filtrate is poured into water, extracted with diethyl ether, washed with brine, dried and concentrated *in vacuo*. Flash chromatography (silica gel, hexane/ethyl acetate 6/4) affords 4"-deoxy-4"-(*S*)-(2-oxo-propyl)-avermectin B_1 (compound 4.7)

4"-Deoxy-4"-(*S*)-(2-oxo-propyl)-avermectin B_1 : $C_{51}H_{76}O_{14}$, MW: 913.2. LCMS: B_{1a}: 10.56 min., 935.5 (M+Na). 1H NMR (500 MHz, $CDCl_3$) selected data, δH (ppm): 3.44 (s, 3H, OCH_3), 3.27 (s, 3H, OCH_3), 2.05 (s, 3H, $CH_3C=O$).

Example P9: 4"-Deoxy-4"-(*S*)-(2-Hydroxy-2-methyl-propyl)-Avermectin B_1

A solution of 4"-deoxy-4"-(*S*)-(2-oxo-propyl)-avermectin B_1 (108 mg) in tetrahydrofuran (5 ml) at –10°C is treated with methylmagnesium bromide (3M in diethyl ether, 0.13 ml). The mixture is stirred at room temperature for 1 hour, quenched by the addition of sat. NH_4Cl, extracted with ethyl acetate, washed with brine, dried and concentrated. Flash chromatography (silica gel, hexane/ethyl acetate 6/4) affords 4"-deoxy-4"-(*S*)-(2-hydroxy-2-methyl-propyl)-Avermectin B_1 (56%). (compound 2.17)

4"-Deoxy-4"-(*S*)-(2-hydroxy-2-methyl-propyl)-Avermectin B_1: $C_{52}H_{80}O_{14}$, MW: 928.6. LCMS: t_{RT}, B_{1a}: 13.46 min., 951.5 (M+Na), 929.6 (M+H).

Example P10: 4"-Deoxy-4"-(*R*)-(3-Hydroxymethyl)-Avermectin B_1

Step A: Diiodomethane (0.4 ml) is added to a rapidly stirred suspension of zinc dust (0.6 g) in tetrahydrofuran (10 ml). The mixture is stirred 45 min. at room temperature, then cooled to 0°C. Titanium tetrachloride (1M in CH_2Cl_2, 1 ml) is added and the resulting dark brown solution stirred 30 min. at room temperature. 5-O-*tert*-butyldimethylsilyl-4"-oxo-avermectin B1 (985 mg) in tetrahydrofuran (5 ml) is added dropwise and the reaction mixture stirred for 10 min at room temperature, added *via* syringe to a stirred mixture of sat. $NaHCO_3$ (50 ml) and ethyl acetate (50 ml). The organic layer is washed with brine, dried over Na_2SO_4, and concentrated. Flash chromatography of the residue (silica gel, hexane/ethyl acetate 7/3) affords 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-*exo*-methylene-avermectin B_1.

Step B: 300 mg of 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-*exo*-methylene-avermectin B_1 is treated as described in Example P.5, Step A, affording after flash chromatography (silica gel, hexane/ethyl acetate 7/3) 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-(*R*)-(3-hydroxymethyl)-Avermectin B_1.

Step C: 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-(*R*)-(3-hydroxymethyl)-Avermectin B_1 obtained in step B is treated as described in Example P.1, Step C affording 4"-deoxy-4"-(*R*)-(3-hydroxymethyl)-avermectin B_1.

4"-Deoxy-4"-(*R*)-(3-hydroxymethyl)-avermectin B_1: $C_{49}H_{74}O_{14}$, MW: 886.5. LCMS: t_{RT}, B_{1a}: 8.85 min., 909 (M+Na); 1H NMR (500 MHz, $CDCl_3$) selected data, δH (ppm): 2.15 (m,

1H, CH-4"), 3.03 (br, 1H, CH_2OH), 3.43 (s, 3H, OCH_3), 3.45 (s, 3H, OCH_3), 3.84 (m, 1H, CH_2OH), 4.06 (m, 1H, CH_2OH).

Example P11: 4"-Deoxy-4"-(*S*)-Cyano-Avermectin B_1

Step A: 5-O-*tert*-Butyldimethylsilyl-4"-deoxy-4"-(*R*)-trifluoromethanesulfonyloxy-avermectin B_1 (500 mg) is dissolved in N,N-Dimethylformamide (10 ml). The solution is cooled to –40°C then tetrabutylammonium cyanide (240 mg) is added in one portion. The orange solution is slowly warmed to room temperature and stirred at this temperature for 6h. The reaction mixture is poured into water, extracted with ethyl acetate, washed with water, sat. NH_4Cl, dried over Na_2SO_4, dried over Na_2SO_4 and concentrated providing 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-(*S*)-cyano-Avermectin B_1.

Step B: Crude 5-O-*tert*-butyldimethylsilyl-4"-deoxy-4"-(*S*)-cyano-avermectin B_1 of step A is treated as described in Example P.1, Step C affording after flash-chromatography (silica gel, hexane/ethyl acetate 7/3) 4"-deoxy-4"-(*S*)-cyano-Avermectin B_1 (compound 3.26).

4"-Deoxy-4"-(*S*)-cyano-avermectin B_1: $C_{49}H_{71}NO_{13}$, MW: 881.5. LCMS: t_{RT}, B_{1a}: 10.17 min., 904 (M+Na), 882.5 (M+H); 1H NMR (500 MHz, $CDCl_3$) selected data, δH (ppm): 2.28 (m, 1H, CH-4"), 3.22 (t, J = 8.5 Hz, 1H, CH-4'), 3.31 (dd, J= 2.2, 3.8 Hz, 1H, CH-2), 3.44 (s, 3H, OCH_3), 3.52 (s, 3H, OCH_3), 3.75 (dq, J = 10.3, 6.2 Hz, 1H, CH-5"), 3.95 (s, 1H, CH-13), 3.98 (d, 1H, J = 5.4 Hz, CH-6), 4.02 (s, 1H, 7-OH), 4.30 (m, 1H, CH-5), 5.43 (s, 1H, CH-3).

Example P12: 4"-Deoxy-Avermectin B_1-4"-(*S*)-Dimethylmalonate

Step A: Dimethylmalonate (0.08 ml) is added to a suspension of sodium hydride (60% in oil, 22 mg) in N,N-dimethylformamide (10 ml) at 0°C, and the mixture was stirred at this temperature for 10 min. 5-O-*tert*-butyldimethylsilyl-4"-*epi*-Avermectin B_1-trifluoromethane-sulfonate (500 mg) in N,N-dimethylformamide (5 ml) is then added dropwise, and the resulting orange solution is stirred at 50°C for 1 hours. Water is added, and the mixture is extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated. Flash chromatography (silica gel, hexane/ethyl acetate 9/1) 5-O-*tert*-butyldimethylsilyl-4"-deoxy-avermectin B_1-4"-(*S*)-dimethylmalonate.

Step B: 5-O-*tert*-butyldimethylsilyl-4"-deoxy-Avermectin B_1-4"-(*S*)-dimethylmalonate is treated as described in Example P.1, Step C to give 4"-deoxy-Avermectin B_1-4"-(*S*)-dimethylmalonate (compound 3.1).

4"-Deoxy-avermectin B_1-4"-(*S*)-dimethylmalonate: $C_{53}H_{78}O_{17}$, MW: 986.5. LCMS: t_{RT}, B_{1a}: 9.89 min., 1009.4 (M+Na).

Example P13: 4'-Deoxy-4'-(β)-Allyl-Avermectin B_1 Monosaccharide

Step A: To a solution of 5-O-*tert*-butyldimethylsilyl-avermectin B_1 monosaccharide (0.84 g) in N,N-dimethylformamide (5 ml) at room temprature is added 1,1'-thiocarbonyl diimidazole (0.53 g). The reaction mixture is stirred at 60°C for 4 hours and on cooling to room temperature it is diluted with ethyl acetate and poured into water. Extraction of the aqueous phase with ethyl acetate is followed by drying over $MgSO_4$, and concentration *in vacuo*. Flash chromatography (silica gel, hexane/ethyl acetate 9/1) of the crude residue affords 4'-O-(imidazolethionocarbonyl)-5-O-*tert*-butyldimethylsilyl avermectin B_1 which is characterized by its mass and nmr spectra.

Step B: A degassed solution of the 4'-O-(imidazolethionocarbonyl)-5-O-*tert*-butyldimethylsilyl avermectin B_1 (953 mg, 1.0 mmol) in toluene (10 ml) is treated with allyltributyltin (1.24 ml, 4.0 mmol) and α,α'-azoisobutyronitrile (131 mg, 0.8 mmol) and the solution is stirred at 85°C for 1.5 hours. The reaction mixture is diluted with ethyl acetate and poured into water. Extraction of the aqueous phase with ethyl acetate is followed by drying over $MgSO_4$ and concentrating *in vacuo*. The crude residue is purified by flash chromatography (silica gel, hexane/ethyl acetate 9/1) affording 5- O-*tert*-butyldimethylsilyl-4"-deoxy-4"-(*S*)-allyl-avermectin B_1 monosaccharide which is characterized by its mass and nmr spectra.

Step C: To a solution of 5-O-*tert*-butyldimethylsilyl-4'-O-(*S*)-allyl-avermectin B_1 monosaccharide (231 mg) in methanol (5 ml) at 0 °C is added methanesulphonic acid (0.02 ml). The reaction mixture is stirred for 4 hours and is then poured into saturated sodium bicarbonate, extracted with ethyl acetate, dried over Mg_2SO_4, and concentrated *in vacuo*. Flash chromatography (silica gel, hexane/ethyl acetate 3/0) affords 4'-O-(*S*)-allyl-avermectin B_1 monosaccharide which is characterized by its mass and nmr spectra (compound 5,2).

4'-O-(*S*)-Allyl-avermectin B_1 monosaccharide: B_{1a} $C_{44}H_{64}O_{10}$, MW: 752.5. LCMS: t_{RT},: 10.45 min., 775.4 (M+Na); B_{1b} $C_{43}H_{62}O_{10}$, MW: 738.4. LCMS: t_{RT},: 9.76 min., 961.4 (M+Na).

Example P14: 4'-Deoxy-4'-(*S*)-(2-oxo-propyl)-Avermectin B_1

Step A: A suspension of 150 mg of 5-O-*tert*-butyldimethylsilyl-4'-deoxy-4'-(*S*)-allyl-avermectin B_1 in a mixture of N,N-dimethylacetamide/water (0.35ml, 7/1) is treated with 5 mg palladium dichloride and 7 mg copper (II) acetate hydrate. The mixture is placed under oxygen at 1 atm and stirred for 48 hours. The mixture is diluted with diethyl ether and filtered through celite. The filtrate is poured into water, extracted with diethyl ether, washed with brine, dried and concentrated *in vacuo*. Flash chromatography (silica gel, hexane/ethyl

acetate 6/4) affords 5-O-*tert*-butyldimethylsilyl-4'-deoxy-4'-(*S*)-(2-oxo-propyl)-avermectin B_1 which is characterized by its mass and nmr spectra.

4"-deoxy-4"-(*S*)-(2-oxo-propyl)-avermectin B_1 : $C_{51}H_{76}O_{14}$, MW: 913.2. LCMS: B_{1a}: 10.56 min., 935.5 (M+Na). 1H NMR (500 MHz, $CDCl_3$) selected data, δH (ppm): 3.44 (s, 3H, OCH_3), 3.27 (s, 3H, OCH_3), 2.05 (s, 3H, $CH_3C=O$).

Step B: 5-O-*tert*-butyldimethylsilyl-4'-deoxy-4'-(*S*)-(2-oxo-propyl)-avermectin B_1 of step A is treated as described in Example P1, Step C affording after flash-chromatography (silica gel, hexane/ethyl acetate 3/2) 4'-deoxy-4'-(*S*)-(2-oxo-propyl)-avermectin B_1 which is characterized by its mass and nmr spectra (compound 4.8).

4'-Deoxy-4'-(*S*)-(2-oxo-propyl)-avermectin B_1 : $C_{44}H_{64}O_{11}$, MW: 768.4. LCMS: B_{1a}: 8.48 min., 791.5 (M+Na); B_{1b} $C_{43}H_{62}O_{11}$, MW: 754.4. LCMS: t_{RT}: 7.84 min., 777.4 (M+Na).

Similarly to the preparation examples above it is also possible to prepare the corresponding compounds listed in Tables 1 to 8. In addition, the remaining compounds listed in Tables 1 to 9 may be prepared by methods known to those skilled in the art.

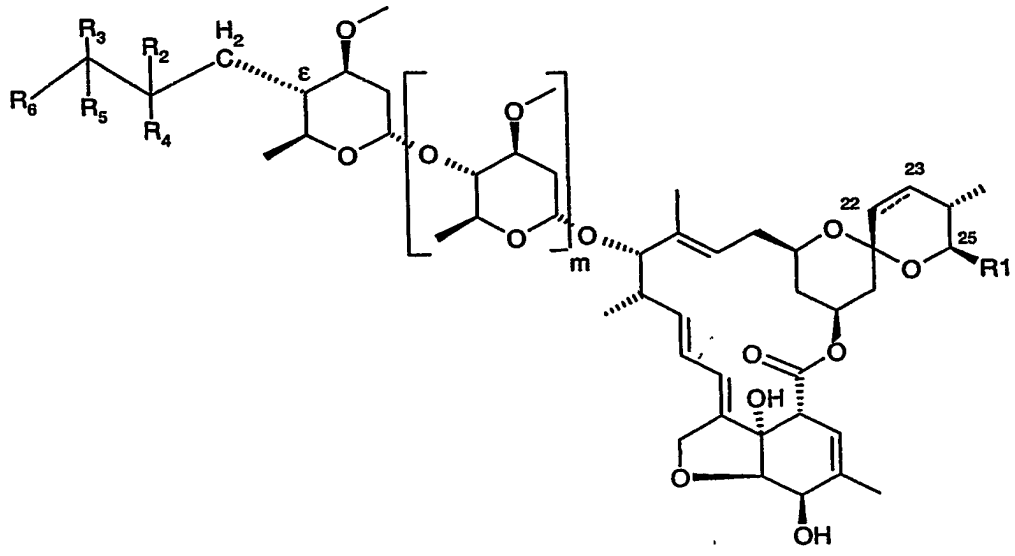
Since in most cases the compounds are present as mixtures of the avermectin derivatives B1a and B1b, characterization by customary physical data such as melting point or refractive index makes little sense. For this reason, the compounds are characterized by the retention times which are determined in an analysis by HPLC (high performance liquid chromatography). Here, the term B1a refers to the main component in which R_1 is sec-butyl, with a content of usually more than 80%. B1b denotes the minor component in which R_1 is isopropyl. The compounds where two retention times are given both for the B1a and for the B1b derivative are mixtures of diastereomers which can be separated chromatographically. In the case of compounds where a retention time is given only in column B1a or only in column B1b, the pure B1a or B1b component, respectively, can be obtained during work-up. The correct structures of the B1a and B1b components are assigned by mass spectrometry.

The following method is used for HPLC analysis:

HPLC gradient conditions			
Solvent A:	0.01% of trifluoroacetic acid in H_2O		
Solvent B:	0.01% of trifluoroacetic acid in CH_3CN		
Time [min]	A [%]	B [%]	Flow rate [µl/min]
0	80	20	500
0.1	50	50	500
10	5	95	500
15	0	100	500
17	0	100	500
17.1	80	20	500
22	80	20	500
Type of column	YMC-Pack ODS-AQ		
Column length	125 mm		
Internal diameter of column:	2 mm		
Temperature	40°C		

The YMC-Pack ODS-AQ column used for the chromatography of the compounds is manufactured by YMC, Alte Raesfelderstrasse 6, 46514 Schermbeck, Germany.

Table 1: Compounds of the formula

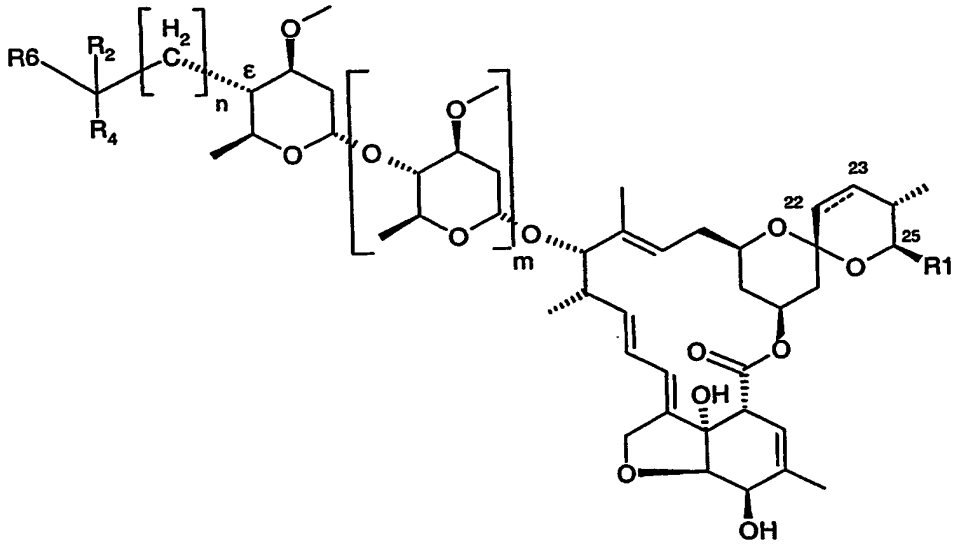


in which R_1 is sec-butyl (B1a) or isopropyl (B1b), and the bond between C_{22} and C_{23} is a double bond

No.	m	R_2	R_3	R_4	R_5	R_6
1.1	1	H	H	H	H	OH
1.2	0	H	H	H	H	OH
1.3	1	OH	H	H	H	OH
1.4	0	OH	H	H	H	OH
1.5	1	H	CH_3	H	H	OH
1.6	0	H	CH_3	H	H	OH
1.7	1	H	CF_3	H	H	OH
1.8	0	H	CF_3	H	H	OH
1.9	1	H	CF_3	H	CH_3	OH
1.10	0	H	CF_3	H	CH_3	OH
1.11	1	H	CH_3	H	CH_3	OH
1.12	0	H	CH_3	H	CH_3	OH
1.13	0	H	H	H	H	$OC(O)NH_2$
1.14	1	H	H	H	H	OC(O)NHMe
1.15	0	H	H	H	H	OC(O)NHMe
1.16	1	H	H	H	H	OC(S)NHMe
1.17	0	H	H	H	H	OC(S)NHMe
1.18	1	H	H	H	H	$C(O)CF_3$
1.19	0	H	H	H	H	$C(O)CF_3$
1.20	1	H	H	H	H	$OC(O)CH_3$
1.21	0	H	H	H	H	$OC(O)CH_3$
1.22	1	H	H	H	H	$SC(O)CH_3$
1.23	0	H	H	H	H	$SC(O)CH_3$
1.24	1	H	H	H	H	OCH_3
1.25	0	H	H	H	H	OCH_3
1.26	1	H	H	H	H	OCH_2OCH_3
1.27	0	H	H	H	H	OCH_2OCH_3
1.28	1	H	H	H	H	ONH_2
1.29	0	H	H	H	H	ONH_2
1.30	1	H	H	H	H	N_3
1.31	0	H	H	H	H	N_3

No.	m	R_2	R_3	R_4	R_5	R_6
1.32	1	H	H	H	H	NHCHO
1.33	0	H	H	H	H	NHCHO
1.34	1	H	H	H	H	$NHCO_2CH_3$
1.35	0	H	H	H	H	$NHCO_2CH_3$
1.36	1	H	H	H	H	$NH(C=O)CH_2OCH_3$
1.37	0	H	H	H	H	$NH(C=O)CH_2OCH_3$
1.38	1	H	H	H	H	NH_2
1.39	0	H	H	H	H	NH_2
1.40	1	H	H	H	H	$NHCH_2COCH_3$
1.41	0	H	H	H	H	$NHCH_2COCH_3$
1.42	1	H	H	H	H	NHOH
1.43	0	H	H	H	H	NHOH
1.44	1	H	H	H	H	$NHOCH_3$
1.45	0	H	H	H	H	$NHOCH_3$
1.46	1	H	H	H	H	NCH_3OH
1.47	0	H	H	H	H	NCH_3OH
1.48	1	H	H	H	H	NCH_3OH
1.49	0	H	H	H	H	NCH_3OH
1.50	1	H	H	H	H	$NH(C=O)OCH_3$
1.51	0	H	H	H	H	$NH(C=O)OCH_3$
1.52	1	H	H	H	H	Cl
1.53	0	H	H	H	H	Cl

Table 2: Compounds of the formula



in which R_1 is sec-butyl (B1a) or isopropyl (B1b), and the bond between C_{22} and C_{23} is a double bond

No.	m	n	R_2	R_4	R_6
2.1	1	1	H	H	OH
2.2	0	1	H	H	OH
2.3	1	0	H	H	OH
2.4	0	0	H	H	OH
2.5	1	1	H	CH_3	OH
2.6	0	1	H	CH_3	OH
2.7	1	0	H	CH_3	OH
2.8	0	0	H	CH_3	OH
2.9	1	1	H	CF_3	OH
2.10	0	1	H	CF_3	OH
2.11	1	0	H	CF_3	OH
2.12	0	0	H	CF_3	OH
2.13	1	1	CH_3	CF_3	OH
2.14	0	1	CH_3	CF_3	OH
2.15	1	0	CH_3	CF_3	OH
2.16	0	0	CH_3	CF_3	OH
2.17	1	1	CH_3	CH_3	OH
2.18	0	1	CH_3	CH_3	OH

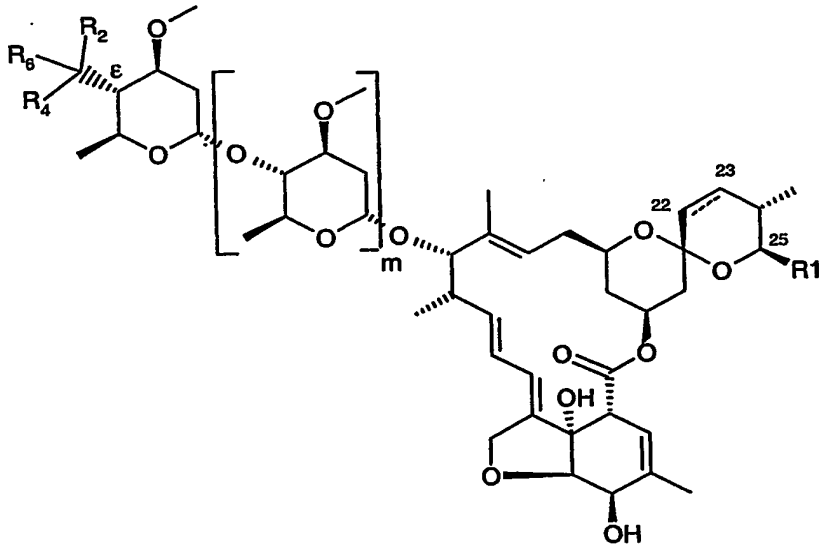
No.	m	n	R_2	R_4	R_6
2.19	1	0	CH_3	CH_3	OH
2.20	0	0	CH_3	CH_3	OH
2.21	1	0	CO_2CH_3	CO_2CH_3	H
2.22	0	0	CO_2CH_3	CO_2CH_3	H
2.23	1	0	CH_2OH	CH_2OH	H
2.24	0	0	CH_2OH	CH_2OH	H
2.25	1	0	CH_3	CH_3	H
2.26	0	0	CH_3	CH_3	H
2.27	1	1	H	H	H
2.28	0	1	H	H	H
2.29	1	1	H	H	SH
2.30	1	0	H	H	SH
2.31	0	1	H	H	SH
2.32	0	0	H	H	SH
2.33	1	1	H	H	SCH_3
2.34	1	0	H	H	SCH_3
2.35	0	1	H	H	SCH_3
2.36	0	0	H	H	SCH_3
2.37	1	1	H	H	$S(O)CH_3$
2.38	1	0	H	H	$S(O)CH_3$
2.39	0	1	H	H	$S(O)CH_3$
2.40	0	0	H	H	$S(O)CH_3$
2.41	1	1	H	H	$S(O)_2CH_3$
2.42	1	0	H	H	$S(O)_2CH_3$
2.43	0	1	H	H	$S(O)_2CH_3$
2.44	0	0	H	H	$S(O)_2CH_3$
2.45	1	1	H	H	$SC(O)CH_3$
2.46	1	0	H	H	$SC(O)CH_3$
2.47	0	1	H	H	$SC(O)CH_3$
2.48	0	0	H	H	$SC(O)CH_3$
2.49	1	1	H	H	N_3
2.50	1	0	H	H	N_3
2.51	0	1	H	H	N_3

No.	m	n	R_2	R_4	R_6
2.52	0	0	H	H	N_3
2.53	1	1	H	H	$OC(O)CH_3$
2.54	1	0	H	H	$OC(O)CH_3$
2.55	0	1	H	H	$OC(O)CH_3$
2.56	0	0	H	H	$OC(O)CH_3$
2.57	1	1	H	H	OCH_2OCH_3
2.58	1	0	H	H	OCH_2OCH_3
2.59	0	1	H	H	OCH_2OCH_3
2.60	0	0	H	H	OCH_2OCH_3
2.61	1	1	H	H	$OS(O)_2NH_2$
2.62	1	0	H	H	$OS(O)_2NH_2$
2.63	0	1	H	H	$OS(O)_2NH_2$
2.64	0	0	H	H	$OS(O)_2NH_2$
2.65	1	1	H	H	$OC(O)NH_2$
2.66	1	0	H	H	$OC(O)NH_2$
2.67	0	1	H	H	$OC(O)NH_2$
2.68	0	0	H	H	$OC(O)NH_2$
2.69	1	1	H	H	OC(O)NHMe
2.70	1	0	H	H	OC(O)NHMe
2.71	0	1	H	H	OC(O)NHMe
2.72	0	0	H	H	OC(O)NHMe
2.73	1	1	H	H	OC(S)NHMe
2.74	1	0	H	H	OC(S)NHMe
2.75	1	1	H	H	C(O)OH
2.76	1	0	H	H	C(O)OH
2.77	0	1	H	H	C(O)OH
2.78	0	0	H	H	C(O)OH
2.79	1	1	H	H	$C(O)NH_2$
2.80	1	0	H	H	$C(O)NH_2$
2.81	0	1	H	H	$C(O)NH_2$
2.82	0	0	H	H	$C(O)NH_2$
2.83	1	1	H	H	$N(CH_3)_2$
2.84	1	0	H	H	$N(CH_3)_2$

No.	m	n	R_2	R_4	R_6
2.85	0	1	H	H	$N(CH_3)_2$
2.86	0	0	H	H	$N(CH_3)_2$
2.87	1	1	H	H	$NHCH_3$
2.88	1	0	H	H	$NHCH_3$
2.89	0	1	H	H	$NHCH_3$
2.90	0	0	H	H	$NHCH_3$
2.91	1	1	H	H	NHCHO
2.92	1	0	H	H	NHCHO
2.93	0	1	H	H	NHCHO
2.94	0	0	H	H	NHCHO
2.95	1	1	H	H	$NHCO_2CH_3$
2.96	1	0	H	H	$NHCO_2CH_3$
2.97	0	1	H	H	$NHCO_2CH_3$
2.98	0	0	H	H	$NHCO_2CH_3$
2.99	1	1	H	H	$NH(C=O)CH_2OCH_3$
2.100	1	0	H	H	$NH(C=O)CH_2OCH_3$
2.101	0	1	H	H	$NH(C=O)CH_2OCH_3$
2.102	0	0	H	H	$NH(C=O)CH_2OCH_3$
2.103	1	1	H	H	NH_2
2.104	1	0	H	H	NH_2
2.105	0	1	H	H	NH_2
2.106	0	0	H	H	NH_2
2.107	1	1	H	H	ONH_2
2.108	1	0	H	H	ONH_2
2.109	0	1	H	H	ONH_2
2.110	0	0	H	H	ONH_2
2.111	1	1	H	H	NHOH
2.112	1	0	H	H	NHOH
2.113	0	1	H	H	NHOH
2.114	0	0	H	H	NHOH
2.115	1	1	H	H	NCH_3OH
2.116	1	0	H	H	NCH_3OH
2.117	0	1	H	H	NCH_3OH

No.	m	n	R_2	R_4	R_6
2.118	0	0	H	H	NCH_3OH
2.119	1	1	H	H	$NH(C=O)OCH_3$
2.120	1	0	H	H	$NH(C=O)OCH_3$
2.121	0	1	H	H	$NH(C=O)OCH_3$
2.122	0	0	H	H	$NH(C=O)OCH_3$
2.123	1	1	H	H	CN
2.124	1	0	H	H	CN
2.125	0	1	H	H	CN
2.126	0	0	H	H	CN
2.127	1	1	H	H	OCH_3
2.128	0	1	H	H	OCH_3
2.129	1	0	H	H	OCH_3
2.130	0	0	H	H	OCH_3
2.131	1	1	H	H	OCH_2SCH_3
2.132	0	1	H	H	OCH_2SCH_3
2.133	1	0	H	H	OCH_2SCH_3
2.134	0	0	H	H	OCH_2SCH_3
2.135	1	1	H	H	$OCH_2OCH_2C_5H_6$
2.136	0	1	H	H	$OCH_2OCH_2C_5H_6$
2.137	1	0	H	H	$OCH_2OCH_2C_5H_6$
2.138	0	0	H	H	$OCH_2OCH_2C_5H_6$
2.139	1	1	H	H	$OCH_2O(CH_2)_2OCH_3$
2.140	0	1	H	H	$OCH_2O(CH_2)_2OCH_3$
2.141	1	0	H	H	$OCH_2O(CH_2)_2OCH_3$
2.142	0	0	H	H	$OCH_2O(CH_2)_2OCH_3$
2.143	1	1	H	H	$NHCH_2COCH_3$
2.144	0	1	H	H	$NHCH_2COCH_3$
2.145	1	0	H	H	$NHCH_2COCH_3$
2.146	0	0	H	H	$NHCH_2COCH_3$

Table 3: Compounds of the formula



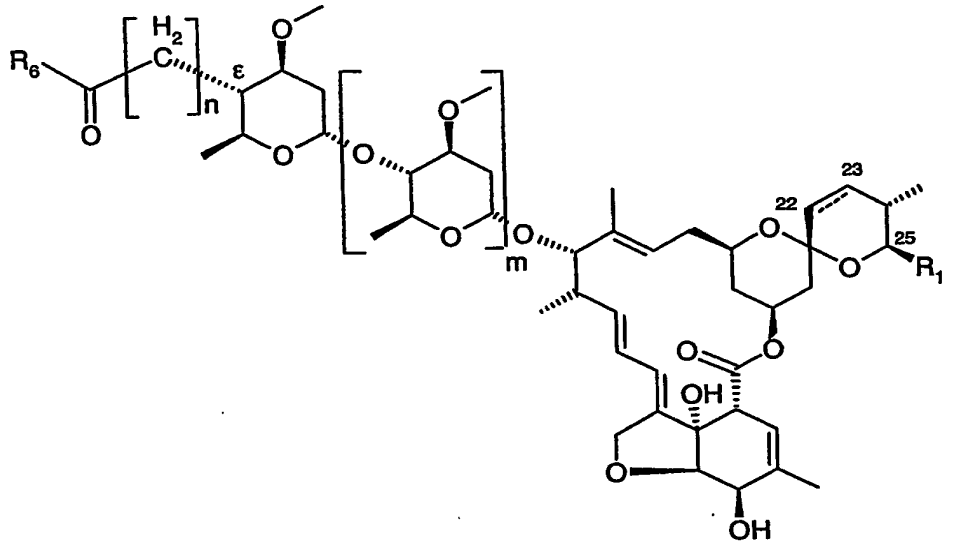
in which R_1 is sec-butyl (B1a) or isopropyl (B1b), and the bond between C_{22} and C_{23} is a double bond

No.	m	R_2	R_4	R_6
3.1	1	CO_2CH_3	CO_2CH_3	H
3.2	1	$CO_2C_6H_5$	$CO_2C_6H_5$	H
3.3	1	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	H
3.4	1	$SO_2C_6H_5$	$SO_2C_6H_5$	H
3.5	1	CN	CN	H
3.6	1	$C(=O)CH_3$	$C(=O)CH_3$	H
3.7	1	C(=O)Ph	$C(=O)C_6H_5$	H
3.8	1	$C(=O)CH_3$	CO_2CH_3	H
3.9	1	$C(=O)CH_3$	$CO_2CH_2CH_3$	H
3.10	1	$C(=O)CH_3$	$CONHC_6H_5$	H
3.11	1	$C(=O)CH_3$	$CONHC(CH_3)_3$	H
3.12	1	$C(=O)CH_2CH_3$	CO_2CH_3	H
3.13	1	$C(=O)CH_2CH_3$	$CONHC_6H_5$	H
3.14	1	$C(=O)CH_2CH_3$	$CONHC(CH_3)_3$	H
3.15	1	CN	CO_2CH_3	H
3.16	1	CN	$CO_2CH_2CH_3$	H
3.17	1	CN	$CONHC_6H_5$	H
3.18	1	NO_2	H	H

No.	m	R_2	R_4	R_6
3.19	1	$C(=O)CH_3$	SC_6H_5	H
3.20	1	$C(=O)CH_3$	SC_6H_5	H
3.21	1	$C(=O)SCH_2CH_3$	$C(=O)SCH_2CH_3$	H
3.22	1	$(O=)COC(CH_3)_2OC(=O)$		H
3.23	1	CN	$SO_2C_6H_5$	H
3.24	1	$C(=O)CF_3$	$CO_2CH_2CH_3$	H
3.25	1	$CO_2CH_2CH_3$	$C(=O)CH_2OCH_3$	H
3.26	1		≡N	
3.27	0	CO_2CH_3	CO_2CH_3	H
3.28	0	$CO_2C_6H_5$	$CO_2C_6H_5$	H
3.29	0	$CO_2CH_2CH_3$	$CO_2CH_2CH_3$	H
3.30	0	$SO_2C_6H_5$	$SO_2C_6H_5$	H
3.31	0	CN	CN	H
3.32	0	$C(=O)CH_3$	$C(=O)CH_3$	H
3.33	0	C(=O)Ph	$C(=O)C_6H_5$	H
3.34	0	$C(=O)CH_3$	CO_2CH_3	H
3.35	0	$C(=O)CH_3$	$CO_2CH_2CH_3$	H
3.36	0	$C(=O)CH_3$	$CONHC_6H_5$	H
3.37	0	$C(=O)CH_3$	$CONHC(CH_3)_3$	H
3.38	0	$C(=O)CH_2CH_3$	CO_2CH_3	H
3.39	0	$C(=O)CH_2CH_3$	$CONHC_6H_5$	H
3.40	0	$C(=O)CH_2CH_3$	$CONHC(CH_3)_3$	H
3.41	0	CN	CO_2CH_3	H
3.42	0	CN	$CO_2CH_2CH_3$	H
3.43	0	CN	$CONHC_6H_5$	H
3.44	0	NO_2	H	H
3.45	0	$C(=O)CH_3$	SC_6H_5	H
3.46	0	$C(=O)CH_3$	SC_6H_5	H
3.47	0	$C(=O)SCH_2CH_3$	$C(=O)SCH_2CH_3$	H
3.48	0	$(O=)COC(CH_3)_2OC(=O)$		H
3.49	0	CN	$SO_2C_6H_5$	H
3.50	0	$C(=O)CF_3$	$CO_2CH_2CH_3$	H
3.51	0	$CO_2CH_2CH_3$	$C(=O)CH_2OCH_3$	H

No.	m	R_2	R_4	R_6
3.52	0		≡N	

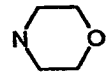
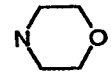
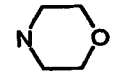
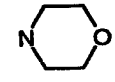
Table 4: Compounds of the formula



in which R_1 is sec-butyl (B1a) or isopropyl (B1b), and the bond between C_{22} and C_{23} is a double bond

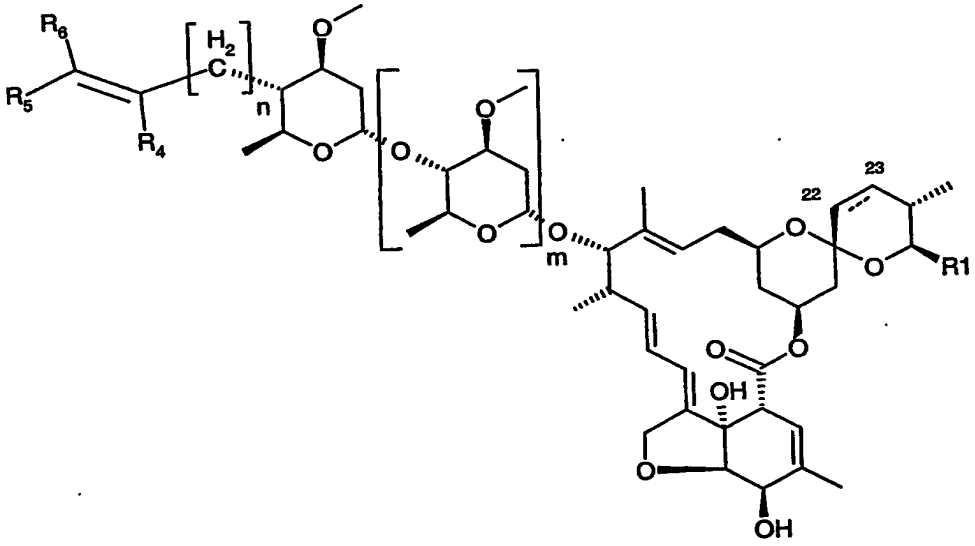
No.	m	n	R_6
4.1	1	1	H
4.2	0	1	H
4.3	1	0	H
4.4	0	0	H
4.5	1	2	H
4.6	0	2	H
4.7	1	1	CH_3
4.8	0	1	CH_3
4.9	1	0	CH_3
4.10	0	0	CH_3
4.11	1	2	CH_3
4.12	0	2	CH_3
4.13	1	1	CH_2CH_3
4.14	0	1	CH_2CH_3
4.15	1	0	CH_2CH_3
4.16	0	0	CH_2CH_3

No.	m	n	R_6
4.17	1	2	CH_2CH_3
4.18	0	2	CH_2CH_3
4.19	1	0	OH
4.20	0	0	OH
4.21	1	1	OH
4.22	0	1	OH
4.23	1	2	OH
4.24	0	2	OH
4.25	1	0	NH_2
4.26	1	1	NH_2
4.27	0	0	NH_2
4.28	0	1	NH_2
4.29	1	2	NH_2
4.30	0	2	NH_2
4.31	1	0	OCH_3
4.32	0	0	OCH_3
4.33	1	1	OCH_3
4.34	0	1	OCH_3
4.35	1	2	OCH_3
4.36	0	2	OCH_3
4.37	1	0	$NHCH_3$
4.38	0	0	$NHCH_3$
4.39	1	1	$NHCH_3$
4.40	0	1	$NHCH_3$
4.41	1	2	$NHCH_3$
4.42	0	2	$NHCH_3$
4.43	1	0	$CH_2CH=CH_2$
4.44	0	0	$CH_2CH=CH_2$
4.45	1	1	$CH_2CH=CH_2$
4.46	0	1	$CH_2CH=CH_2$
4.47	1	2	$CH_2CH=CH_2$
4.48	0	2	$CH_2CH=CH_2$
4.49	1	0	$OCH_2CH_2OCH_3$
4.50	0	0	$OCH_2CH_2OCH_3$
4.51	1	1	$OCH_2CH_2OCH_3$
4.52	0	1	$OCH_2CH_2OCH_3$
4.53	1	0	OC_6H_5

No.	m	n	R_6
4.54	0	0	OC_6H_5
4.55	1	1	OC_6H_5
4.56	0	1	OC_6H_5
4.57	1	0	OC_6H_5
4.58	0	0	OC_6H_5
4.59	1	1	OC_6H_5
4.60	0	1	OC_6H_5
4.61	1	0	
4.62	0	0	
4.63	1	1	
4.64	0	1	
4.65	1	0	
4.66	0	0	
4.67	1	1	
4.68	0	1	
4.69	1	0	F
4.70	0	0	F
4.71	1	1	F
4.72	0	1	F
4.73	1	2	F
4.74	0	2	F
4.75	1	0	Cl
4.76	0	0	Cl
4.77	1	1	Cl
4.78	0	1	Cl
4.79	1	2	Cl

No.	m	n	R_6
4.80	0	2	Cl
4.81	1	0	CF_3
4.82	0	0	CF_3
4.83	1	1	CF_3
4.84	0	1	CF_3
4.85	1	2	CF_3
4.86	0	2	CF_3

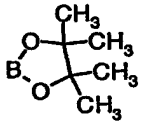
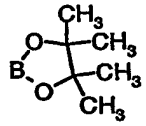
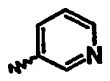
Table 5A: Compounds of the formula



(Id),

in which R_1 is sec-butyl (B1a) or isopropyl (B1b), and the bond between C_{22} and C_{23} is a double bond.

No.	m	n	R_4	R_5	R_6
5.1	1	1	H	H	H
5.2	0	1	H	H	H
5.3	1	2	H	H	H
5.4	0	2	H	H	H
5.5	1	0	H	H	C_6H_5
5.6	0	0	H	H	C_6H_5
5.7	1	1	H	H	CH_2OH
5.8	0	1	H	H	CH_2OH
5.9	1	1	H	H	$CH_2OCH_2OCH_3$

No.	m	n	R_4	R_5	R_6
5.10	0	1	H	H	$CH_2OCH_2OCH_3$
5.11	1	1	H	H	CO_2CH_3
5.12	0	1	H	H	CO_2CH_3
5.13	1	1	H	H	CO_2H
5.14	0	1	H	H	CO_2H
5.15	1	1	H	H	CHO
5.16	0	1	H	H	CHO
5.17	1	1	H	H	CH_2NHCH_3
5.18	0	1	H	H	CH_2NHCH_3
5.19	1	1	H	H	CN
5.20	0	1	H	H	CN
5.21	1	1	H	H	$C(O)CH_3$
5.22	0	1	H	H	$C(O)CH_3$
5.23	1	1	H	H	$C(O)C_6H_5$
5.24	1	1	H	H	CH_2Oac
5.25	0	1	H	H	CH_2Oac
5.26	1	1	H	H	
5.27	0	1	H	H	
5.28	1	1	H	H	$Si(OEt)_3$
5.29	0	1	H	H	$Si(OEt)_3$
5.30	1	1	H	H	$C(O)C_6H_5$
5.31	0	1	H	H	$C(O)C_6H_5$
5.32	1	1	H	H	CH_2Cl
5.33	0	1	H	H	CH_2Cl
5.34	1	1	H	H	$P(O)(OEt)_2$
5.35	0	1	H	H	$P(O)(OEt)_2$
5.36	1	1	H	H	$CH_2P(O)(OEt)_2$
5.37	0	1	H	H	$CH_2P(O)(OEt)_2$
5.38	1	1	H	H	$S(O)_2C_6H_5$
5.39	0	1	H	H	$S(O)_2C_6H_5$
5.40	1	1	H	H	

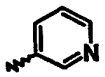
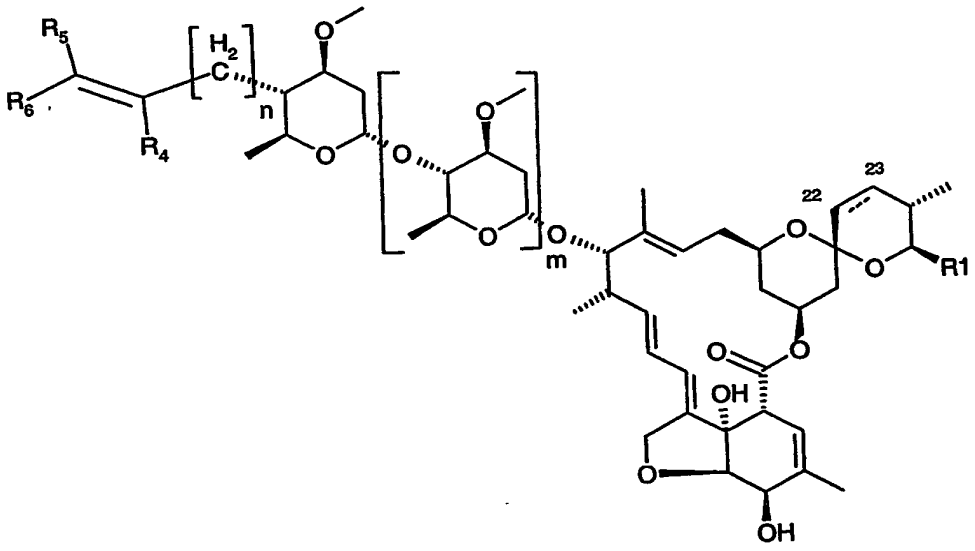
No.	m	n	R_4	R_5	R_6
5.41	1	1	H	H	
5.42	0	1	H	H	
5.43	0	1	H	H	
5.44	1	1	H	Cl	Cl
5.45	0	1	H	Cl	Cl
5.46	1	1	H	Br	Br
5.47	0	1	H	Br	Br
5.48	1	1	H	F	F
5.49	0	1	H	F	F

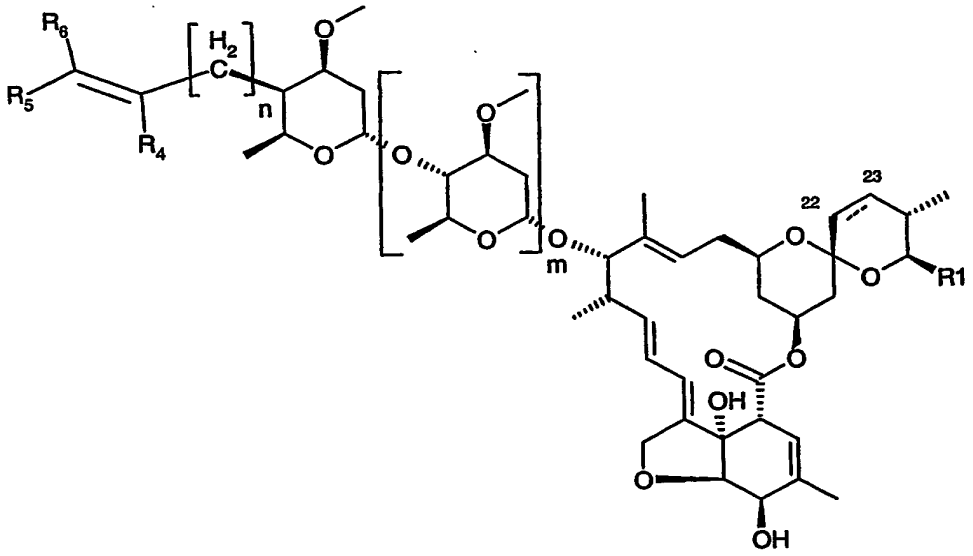
Table 5B: Compounds of the formula



(Idd),

in which R_1 is sec-butyl (B1a) or isopropyl (B1b), and the bond between C_{22} and C_{23} is a double bond and R_4, R_5 and R_6 have the same meanings as in Table 5A.

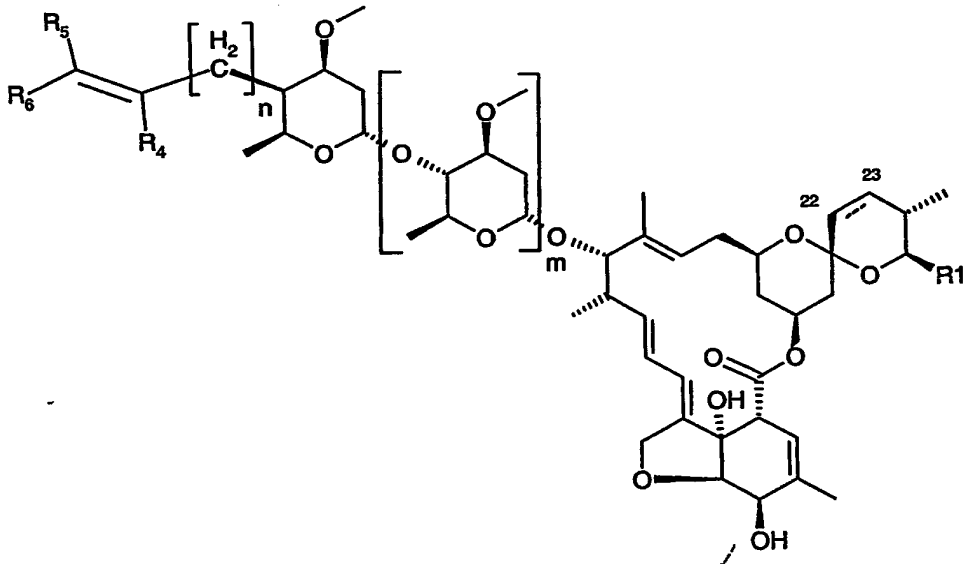
Table 6A: Compounds of the formula



(Id),

in which R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between C_{22} and C_{23} is a double bond, and wherein the combination of m, n, R_4, R_5 and R_6 for each compound corresponds to a line 5.1 to 5.49 of table 5.

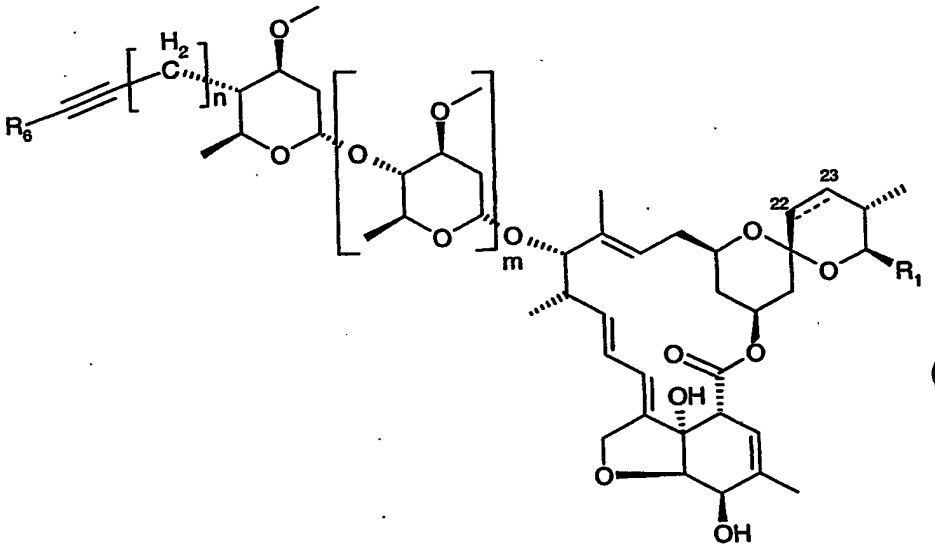
Table 6B: Compounds of the formula



(Idd),

in which R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between C_{22} and C_{23} is a double bond, and wherein the combination of m, n, R_4, R_5 and R_6 for each compound corresponds to a line 5.1 to 5.49 of table 5.

Table 7: Compounds of the formula



(Im),

in which R_1 is sec-butyl (B1a) or isopropyl (B1b), and the bond between C_{22} and C_{23} is a double bond

	M	n	R_6
7.1	1	0	H
7.2	0	0	H
7.3	1	1	H
7.4	0	1	H
7.5	1	2	H
7.6	0	2	H
7.7	1	0	C_6H_5
7.8	0	0	C_6H_5
7.9	1	1	C_6H_5
7.10	0	1	C_6H_5
7.11	1	0	$C(=O)CH_3$
7.12	0	0	$C(=O)CH_3$
7.13	1	1	$C(=O)CH_3$
7.14	0	1	$C(=O)CH_3$
7.15	1	0	CH_2OH
7.16	0	0	CH_2OH
7.17	1	1	CH_2OH
7.18	0	1	CH_2OH
7.19	1	0	$C(=O)NHCH_3$

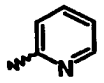
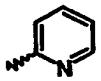
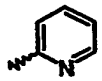
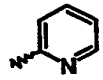
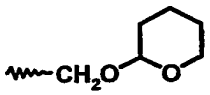
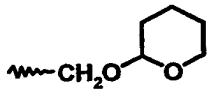
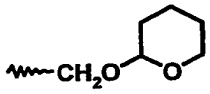
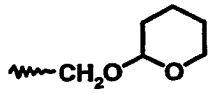
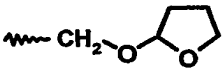
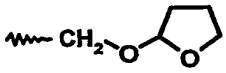
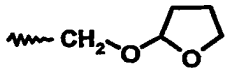
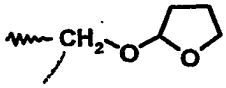
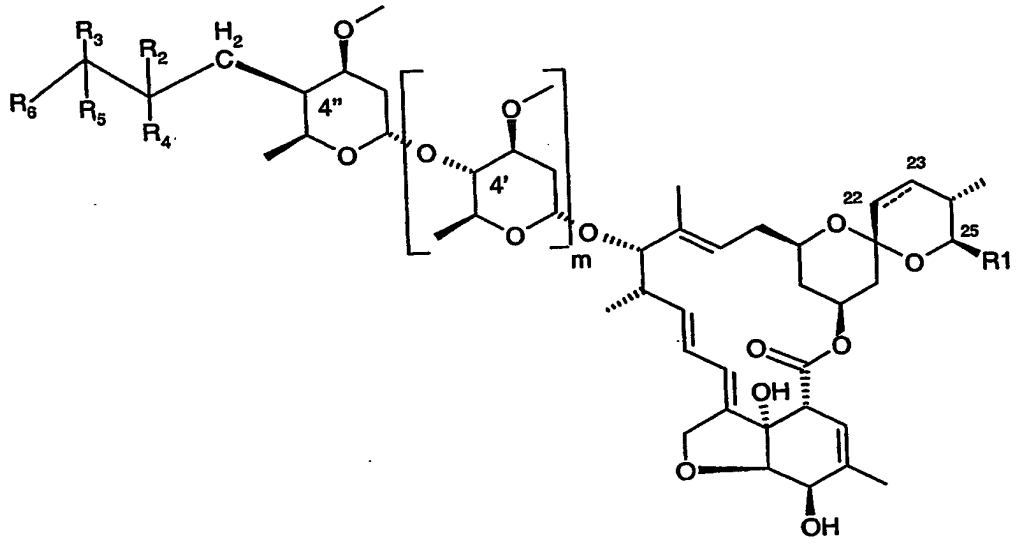
	M	n	R_6
7.20	0	0	$C(=O)NHCH_3$
7.21	1	1	$C(=O)NHCH_3$
7.22	0	1	$C(=O)NHCH_3$
7.23	1	0	
7.24	0	0	
7.25	1	1	
7.26	0	1	
7.27	1	0	
7.28	0	0	
7.29	1	1	
7.30	0	1	
7.31	1	0	
7.32	0	0	
7.33	1	1	
7.34	0	1	

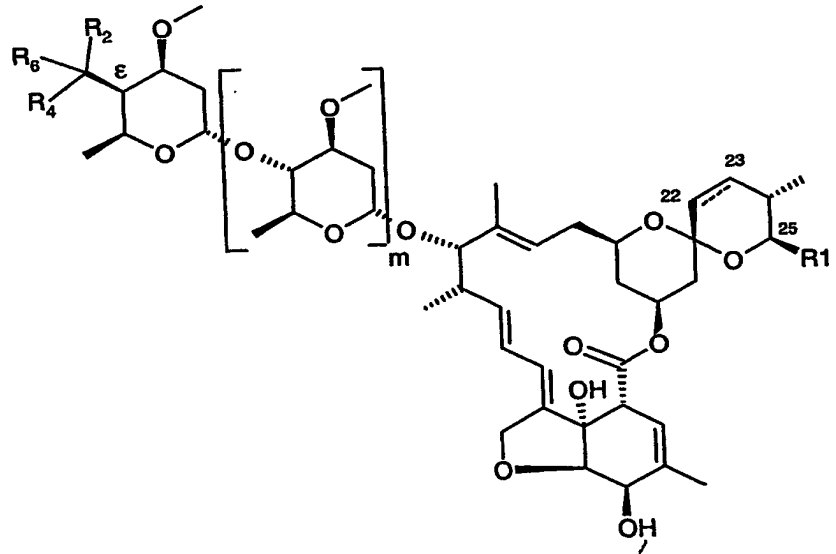
Table 8: Compounds of the formula



(Ii)

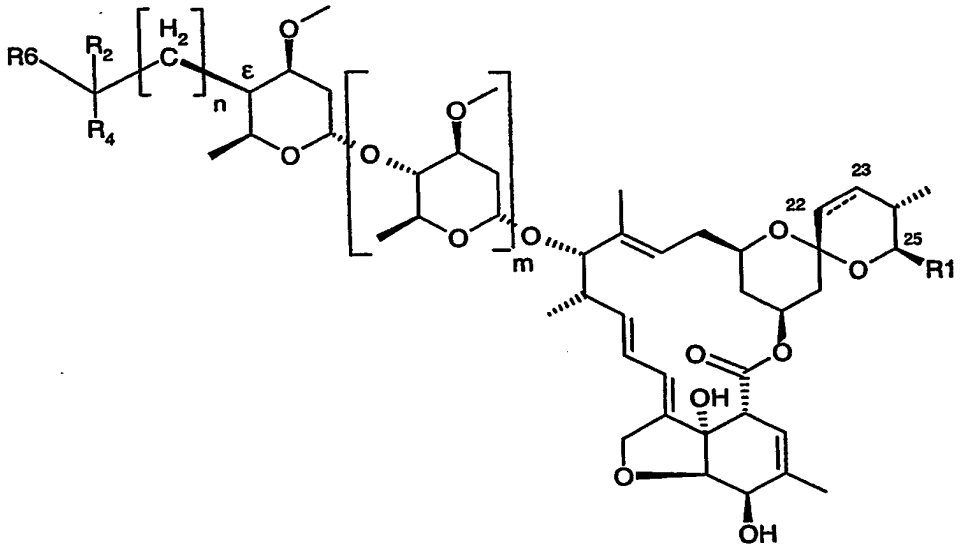
in which R_1 is sec-butyl (B1a) or isopropyl (B1b), and the bond between C_{22} and C_{23} is a double bond and wherein the combination of m, n, R_2, R_3, R_4, R_5 and R_6 for each compound corresponds to a line 1.1 to 1.52 of table 1.

Table 9: Compounds of the formula



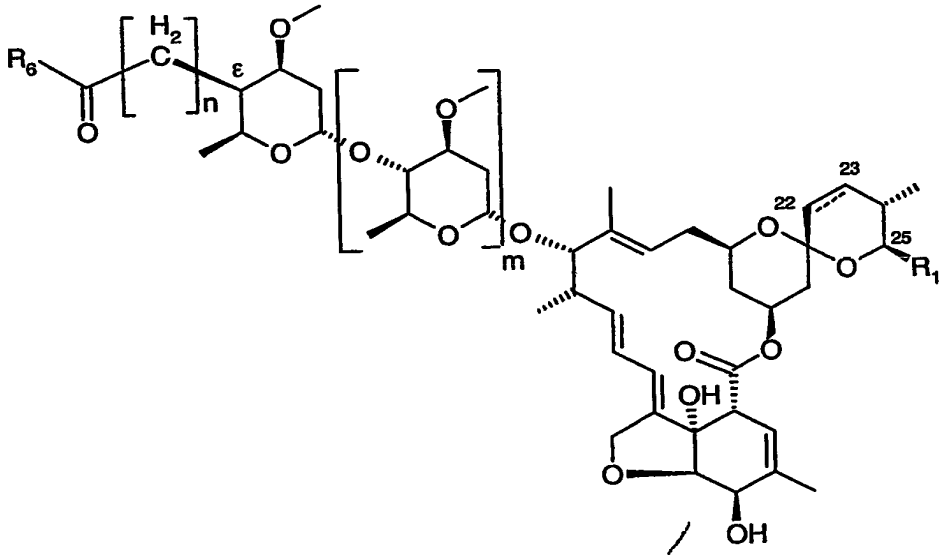
in which R_1 is sec-butyl (B1a) or isopropyl (B1b), and the bond between C_{22} and C_{23} is a double bond and wherein the combination of m, R_2, R_4 and R_6 for each compound corresponds to a line 3.1 to 3.52 of table 3.

Table 10: Compounds of the formula



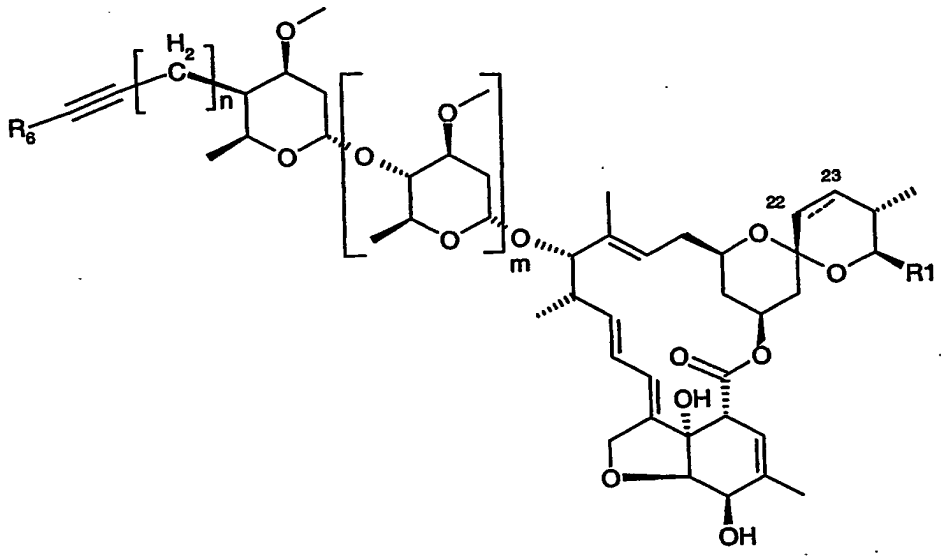
in which R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between C_{22} and C_{23} is a double bond and the and wherein the combination of m, n, R_2, R_4 and R_6 for each compound corresponds to a line 2.1 to 2.146 of table 2.

Table 11: Compounds of the formula



in which R_1 is sec-butyl (B1a) or isopropyl (B1b), and the bond between C_{22} and C_{23} is a double bond and m, n and R_6 for each compound corresponds to a line 4.1 to 4.86 of table 4.

Table 12: Compounds of the formula



in which R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between C_{22} and C_{23} is a double bond, m and n and R_6 for each compound corresponds to a line 7.1 to 7.34 of table 7.

Table 13: Compounds of the formula as in table 1 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, R_2, R_3, R_4, R_5 and R_6 for each compound corresponds to a line 1.1 to 1.53 of table 1.

Table 14: Compounds of the formul a as in table 1 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, R_2, R_3, R_4, R_5 and R_6 for each compound corresponds to a line 1.1 to 1.53 of table 1.

Table 15: Compounds of the formula as in table 1 in which R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between C_{22} and C_{23} is a single bond, and the combination of m, R_2, R_3, R_4, R_5 and R_6 for each compound corresponds to a line 1.1 to 1.53 of table 1.

Table 16: Compounds of the formula as in table 1 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, R_2, R_3, R_4, R_5 and R_6 for each compound corresponds to a line 1.1 to 1.53 of table 1.

Table 17: Compounds of the formula as in table 1 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, R_2, R_3, R_4, R_5 and R_6 for each compound corresponds to a line 1.1 to 1.53 of table 1.

Table 18: Compounds of the formula as in table 2 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, n, R_2, R_4, and R_6 for each compound corresponds to a line 2.1 to 2.146 of table 2.

Table 19: Compounds of the formula as in table 2 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, n, R_2, R_4, and R_6 for each compound corresponds to a line 2.1 to 2.146 of table 2.

Table 20: Compounds of the formula as in table 2 in which R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between C_{22} and C_{23} is a single bond, and the combination of m, n, R_2, R_4, and R_6 for each compound corresponds to a line 2.1 to 2.146 of table 2.

Table 21: Compounds of the formula as in table 2 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, n, R_2, R_4, and R_6 for each compound corresponds to a line 2.1 to 2.146 of table 2.

Table 22: Compounds of the formula as in table 2 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, n, R_2, R_4, and R_6 for each compound corresponds to a line 2.1 to 2.146 of table 2.

Table 23: Compounds of the formula as in table 3 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, R_2, R_4, and R_6 for each compound corresponds to a line 3.1 to 3.52 of table 3.

Table 24: Compounds of the formula as in table 3 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, R_2, R_4, and R_6 for each compound corresponds to a line 3.1 to 3.52 of table 3.

Table 25: Compounds of the formula as in table 3 in which R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between C_{22} and C_{23} is a single bond, and the combination of m, R_2, R_4, and R_6 for each compound corresponds to a line 3.1 to 3.52 of table 3.

Table 26: Compounds of the formula as in table 3 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, R_2, R_4, and R_6 for each compound corresponds to a line 3.1 to 3.52 of table 3.

Table 27: Compounds of the formula as in table 3 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, R_2, R_4, and R_6 for each compound corresponds to a line 3.1 to 3.52 of table 3.

Table 28: Compounds of the formula as in table 4 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, n and R_6 for each compound corresponds to a line 4.1 to 4.86 of table 4.

Table 29: Compounds of the formula as in table 4 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, n and R_6 for each compound corresponds to a line 4.1 to 4.86 of table 4.

Table 30: Compounds of the formula as in table 4 in which R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between C_{22} and C_{23} is a single bond, and the combination of m, n and R_6 for each compound corresponds to a line 4.1 to 4.86 of table 4.

Table 31: Compounds of the formula as in table 4 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, n and R_6 for each compound corresponds to a line 4.1 to 4.86 of table 4.

Table 32: Compounds of the formula as in table 4 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, n and R_6 for each compound corresponds to a line 4.1 to 4.86 of table 4.

Table 33: Compounds of the formula as in table 5 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, n, R_4, R_5 and R_6 for each compound corresponds to a line 5.1 to 5.49 of table 5.

Table 34: Compounds of the formula as in table 5 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, n, R_4, R_5 and R_6 for each compound corresponds to a line 5.1 to 5.49 of table 5.

Table 35: Compounds of the formula as in table 5 in which R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between C_{22} and C_{23} is a single bond, and the combination of m, n, R_4, R_5 and R_6 for each compound corresponds to a line 5.1 to 5.49 of table 5.

Table 36: Compounds of the formula as in table 5 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, n, R_4, R_5 and R_6 for each compound corresponds to a line 5.1 to 5.49 of table 5.

Table 37: Compounds of the formula as in table 5 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, n, R_4, R_5 and R_6 for each compound corresponds to a line 5.1 to 5.49 of table 5.

Table 38: Compounds of the formula as in table 6 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, n, R_4, R_5 and R_6 for each compound corresponds to a line 5.1 to 5.49 of table 5.

Table 39: Compounds of the formula as in table 6 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, n, R_4, R_5 and R_6 for each compound corresponds to a line 5.1 to 5.49 of table 5.

Table 40: Compounds of the formula as in table 6 in which R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between C_{22} and C_{23} is a single bond, and the combination of m, n, R_4, R_5 and R_6 for each compound corresponds to a line 5.1 to 5.49 of table 5.

Table 41: Compounds of the formula as in table 6 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, n, R_4, R_5 and R_6 for each compound corresponds to a line 5.1 to 5.49 of table 5.

Table 42: Compounds of the formula as in table 6 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, n, R_4, R_5 and R_6 for each compound corresponds to a line 5.1 to 5.49 of table 5.

Table 43: Compounds of the formula as in table 7 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, n and R_6 for each compound corresponds to a line 7.1 to 7.34 of table 7.

Table 44: Compounds of the formula as in table 7 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, n and R_6 for each compound corresponds to a line 7.1 to 7.34 of table 7.

Table 45: Compounds of the formula as in table 7 in which R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between C_{22} and C_{23} is a single bond, and the combination of m, n and R_6 for each compound corresponds to a line 7.1 to 7.34 of table 7.

Table 46: Compounds of the formula as in table 7 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, n and R_6 for each compound corresponds to a line 7.1 to 7.34 of table 7.

Table 47: Compounds of the formula as in table 7 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, n and R_6 for each compound corresponds to a line 7.1 to 7.34 of table 7.

Table 48: Compounds of the formula as in table 8 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, R_2, R_3, R_4, R_5 and R_6 for each compound corresponds to a line 1.1 to 1.53 of table 1.

Table 49: Compounds of the formula as in table 8 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, R_2, R_3, R_4, R_5 and R_6 for each compound corresponds to a line 1.1 to 1.53 of table 1.

Table 50: Compounds of the formula as in table 8 in which R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between C_{22} and C_{23} is a single bond, and the combination of m, R_2, R_3, R_4, R_5 and R_6 for each compound corresponds to a line 1.1 to 1.53 of table 1.

Table 51: Compounds of the formula as in table 8 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, R_2, R_3, R_4, R_5 and R_6 for each compound corresponds to a line 1.1 to 1.53 of table 1.

Table 52: Compounds of the formula as in table 8 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, R_2, R_3, R_4, R_5 and R_6 for each compound corresponds to a line 1.1 to 1.53 of table 1.

Table 53: Compounds of the formula as in table 9 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, R_2, R_4, and R_6 for each compound corresponds to a line 3.1 to 3.52 of table 3.

Table 54: Compounds of the formula as in table 9 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, R_2, R_4, and R_6 for each compound corresponds to a line 3.1 to 3.52 of table 3.

Table 55: Compounds of the formula as in table 9 in which R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between C_{22} and C_{23} is a single bond, and the combination of m, R_2, R_4, and R_6 for each compound corresponds to a line 3.1 to 3.52 of table 3.

Table 56: Compounds of the formula as in table 9 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, R_2, R_4, and R_6 for each compound corresponds to a line 3.1 to 3.52 of table 3.

Table 57: Compounds of the formula as in table 9 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, R_2, R_4, and R_6 for each compound corresponds to a line 3.1 to 3.52 of table 3.

Table 58: Compounds of the formula as in table 10 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, n, R_2, R_4, and R_6 for each compound corresponds to a line 2.1 to 2.146 of table 2.

Table 59: Compounds of the formula as in table 10 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, n, R_2, R_4, and R_6 for each compound corresponds to a line 2.1 to 2.146 of table 2.

Table 60: Compounds of the formula as in table 10 in which R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between C_{22} and C_{23} is a single bond, and the combination of m, n, R_2, R_4, and R_6 for each compound corresponds to a line 2.1 to 2.146 of table 2.

Table 61: Compounds of the formula as in table 10 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, n, R_2, R_4, and R_6 for each compound corresponds to a line 2.1 to 2.146 of table 2.

Table 62: Compounds of the formula as in table 10 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, n, R_2, R_4, and R_6 for each compound corresponds to a line 2.1 to 2.146 of table 2.

Table 63: Compounds of the formula as in table 11 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, n and R_6 for each compound corresponds to a line 4.1 to 4.86 of table 4.

Table 64: Compounds of the formula as in table 11 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, n and R_6 for each compound corresponds to a line 4.1 to 4.86 of table 4.

Table 65: Compounds of the formula as in table 11 in which R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between C_{22} and C_{23} is a single bond, and the combination of m, n and R_6 for each compound corresponds to a line 4.1 to 4.86 of table 4.

Table 66: Compounds of the formula as in table 11 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, n and R_6 for each compound corresponds to a line 4.1 to 4.86 of table 4.

Table 67: Compounds of the formula as in table 11 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, n and R_6 for each compound corresponds to a line 4.1 to 4.86 of table 4.

Table 68: Compounds of the formula as in table 12 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, n and R_6 for each compound corresponds to a line 7.1 to 7.34 of table 7.

Table 69: Compounds of the formula as in table 12 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a double bond, and the combination of m, n and R_6 for each compound corresponds to a line 7.1 to 7.34 of table 7.

Table 70: Compounds of the formula as in table 12 in which R_1 is sec-butyl (B1a) or isopropyl (B1b), the bond between C_{22} and C_{23} is a single bond, and the combination of m, n and R_6 for each compound corresponds to a line 7.1 to 7.34 of table 7.

Table 71: Compounds of the formula as in table 12 in which R_1 is cyclohexyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, n and R_6 for each compound corresponds to a line 7.1 to 7.34 of table 7.

Table 72: Compounds of the formula as in table 12 in which R_1 is 1-methyl-butyl, the bond between C_{22} and C_{23} is a single bond, and the combination of m, n and R_6 for each compound corresponds to a line 7.1 to 7.34 of table 7.

Formulation examples for use in crop protection (% = per cent by weight)

Example F1: Emulsion concentrates	a)	b)	c)
Active compound25% 40% 50%			
Calcium dodecylbenzenesulphonate	5%	8%	6%
Castor oil polyethylene glycol ether (36 mol of EO)	5%	-	-
Tributylphenol polyethylene glycol ether (30 mol of EO)	-	12%	4%
Cyclohexanone	-	15%	20%
Xylene mixture	65%	25%	20%

Mixing of finely ground active compound and additives gives an emulsion concentrate which, by dilution with water, affords emulsions of the desired concentration.

Example F2: Solutions	a)	b)	c)	d)
Active compound	80%	10%	5%	95%
Ethylene glycol monomethyl ether	-	20%	-	-
Polyethylene glycol (MW 400)	-	-	70%	-
N-methylpyrrolid-2-one	20%	-	-	-
Epoxidized coconut oil	-	-	-	1%
Petroleum ether (boiling range: 160-190°)	-	-	94%	-

Mixing of finely ground active compound and additives gives a solution suitable for use in the form of microdrops.

Example F3: Granules	a)	b)	c)	d)
Active compound	5%	10%	8%	21%
Kaolin	94%	-	79%	54%
Finely divided silicic acid	1%	-	13%	7%
Attapulgite	-	90%	-	18%

The active compound is dissolved in dichloromethane, the solution is sprayed onto the mixture of carriers and the solvent is evaporated under reduced pressure.

Example F4: Wettable powder	a)	b)	c)
Active compound	25%	50%	75%
Sodium lignosulphonate	5%	5%	-
Sodium lauryl sulphate	3%	-	5%
Sodium diisobutylnaphthalene sulphonate	-	6%	10%
Octylphenol polyethylene glycol ether (7-8 mol of EO)	-	2%	-
Finely divided silicic acid	5%	10%	10%
Kaolin	62%	27%	-

Active compound and additives are mixed and the mixture is ground in a suitable mill. This gives wettable powders which can be diluted with water to give suspensions of the desired concentration.

Example F5: Emulsion concentrate

Active compound	10%
Octylphenol polyethylene glycol ether (4-5 mol of EO)	3%
Calcium dodecylbenzenesulphonate	3%
Castor oil polyethylene glycol ether (36 mol of EO)	4%
Cyclohexanone	30%
Xylene mixture	50%

Mixing of finely ground active compound and additives gives an emulsion concentrate which, by dilution with water, affords emulsions of the desired concentration.

Example F6: Extruder granules

Active compound	10%
Sodium lignosulphonate	2%
Carboxymethylcellulose	1%
Kaolin	87%

Active compound and additives are mixed, the mixture is ground, moistened with water, extruded and granulated, and the granules are dried in a stream of air.

Example 7: Coated granules

Active compound	3%
Polyethylene glycol (MW 200)	3%
Kaolin	94%

In a mixer, the finely ground active compound is applied uniformly to the kaolin which has been moistened with polyethylene glycol. This gives dust-free coated granules.

Example F8: Suspension concentrate

Active compound	40%
Ethylene glycol	10%
Nonylphenol polyethylene glycol ether (15 mol of EO)	6%
Sodium lignosulphonate	10%
Carboxymethylcellulose	1%
Aqueous formaldehyde solution (37%)	0.2%
Aqueous silicone oil emulsion (75%)	0.8%
Water	32%

Mixing of finely ground active compound and additives gives a suspension concentrate which, by dilution with water, affords suspensions of the desired concentration.

Biological examples:

Example B1: Activity against Spodoptera littoralis

Young soya bean plants are sprayed with an aqueous emulsion spray liquor which comprises 12.5 ppm of active compound, and, after the spray coating has dried on, populated with 10 caterpillars of the first stage of Spodoptera littoralis and introduced into a plastic container. 3 days later, the reduction in the population in per cent and the reduction in the feeding damage in per cent (% activity) are determined by comparing the number of dead caterpillars and the feeding damage between the treated and the untreated plants.

In this test, the compounds of the tables show good activity. Thus, in particular the compounds 2.1, 2.2, 2.3, 2.4, 5.1 and 5.2 effect a reduction in the pest population by more than 80%.

Example B2: Activity against Spodoptera littoralis, systemic:

Maize seedlings are placed into the test solution which comprises 12.5 ppm of active compound. After 6 days, the leaves are cut off, placed onto moist filter paper in a Petri dish and populated with 12 to 15 Spodoptera littoralis larvae of the L_1 stage. 4 days later, the reduction of the population in per cent (% activity) is determined by comparing the number of dead caterpillars between the treated and the untreated plants.

In this test, the compounds of the tables show good activity.

Example B3: Activity against Heliothis virescens

35 0- to 24-hour-old eggs of Heliothis virescens are placed onto filter paper in a Petri dish on a layer of synthetic feed. 0.8 ml of the test solution which comprises 12.5 ppm of active compound, is then pipetted onto the filter papers. Evaluation is carried out after 6 days. The reduction in the population in per cent (% activity) is determined by comparing the number of dead eggs and larvae on the treated and the untreated filter papers.

In this test, the compounds of the tables show good activity. Thus, in particular the compounds 2.1, 2.2, 2.3, 2.4, 5.1 and 5.2 effect a reduction in the pest population by more than 80%.

Example B4: Activity against Plutella xylostella caterpillars

Young cabbage plants are sprayed with an aqueous emulsion spray liquor which comprises 12.5 ppm of the active compound. After the spray coating has dried on, the cabbage plants are populated with 10 caterpillars of the first stage of Plutella xylostella and introduced into a plastic container. Evaluation is carried out after 3 days. The reduction in the population in per cent and the reduction in the feeding damage in per cent (% activity) are determined by comparing the number of dead caterpillars and the feeding damage on the treated and the untreated plants.

In this test, the compounds of the tables show good activity against Plutella xylostella. Thus, in particular the compounds 2.1, 2.2, 2.3, 2.4, 5.1 and 5.2 effect a reduction in the pest population by more than 80%.

Example B5: Activity against Frankliniella occidentalis

In Petri dishes, discs of the leaves of beans are placed onto agar and sprayed with test solution which comprises 12.5 ppm of active compound, in a spraying chamber. The leaves are then populated with a mixed population of Frankliniella occidentalis. Evaluation is carried out after 10 days. The reduction in per cent (% activity) is determined by comparing the population on the treated leaves with that of the untreated leaves.

In particular the compounds 2.1, 2.2, 2.3, 2.4, 5.1 and 5.2 effect a reduction in the pest population by more than 80%.

Example B6: Activity against Diabrotica balteata

Maize seedlings are sprayed with an aqueous emulsion spray liquor which comprises 12.5 ppm of active compound and, after the spray coating has dried on, populated with

10 larvae of the second stage of Diabrotica balteata and then introduced into a plastic container. After 6 days, the reduction in the population in per cent (% activity) is determined by comparing the dead larvae between the treated and the untreated plants.

In this test, the compounds of the tables show good activity. Thus, in particular the compounds 2.1, 2.2, 2.3, 2.4, 5.1 and 5.2 effect a reduction in the pest population by more than 80%.

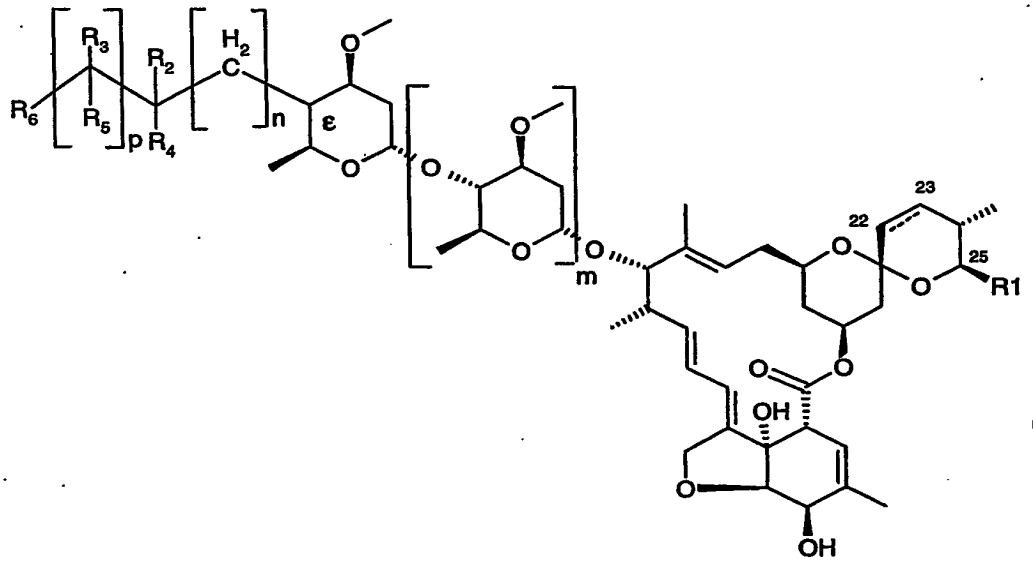
Example B7: Activity against Tetranychus urticae

Young bean plants are populated with a mixed population of Tetranychus urticae and, after 1 day, sprayed with an aqueous emulsion spray liquor which comprises 12.5 ppm of active compound, incubated at 25°C for 6 days and then evaluated. The reduction in the population in per cent (% activity) is determined by comparing the number of dead eggs, larvae and adults on the treated and on the untreated plants.

In this test, the compounds of the tables show good activity. Thus, in particular the compounds 2.1, 2.2, 2.3, 2.4, 5.1 and 5.2 effect a reduction in the pest population by more than 80%.

WHAT IS CLAIMED IS:

1. A compound of the formula



(I),

wherein the bond of atoms C_{22} and C_{23} is a single or double bond;

m is 0 or 1;

n is 0, 1 or 2;

p is 0 or 1;

R_1 is C_1-C_{12}-alkyl, C_3-C_8-cycloalkyl or C_2-C_{12}-alkenyl;

R_2 is H, C_1-C_{12}-alkyl, C_1-C_{12}-haloalkyl, C_1-C_{12}-hydroxyalkyl, OH, halogen, $-N_3$, SCN, NO_2, CN, C_3-C_8cycloalkyl unsubstituted or substituted by from one to three methyl groups, C_3-C_8halocycloalkyl, C_1-C_{12}alkoxy, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_{12}alkenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_2-C_{12}alkynyl, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy, $-P(=O)(OC_1$-$C_6alkyl)_2$, $-Si(C_1$-$C_6alkyl)_3$, $-(CH_2)$-$Si(C_1$-$C_6alkyl)_3$, $-Si(OC_1$-$C_6alkyl)_3$, $-N(R_9)_2$, $-(CH_2)$-$N(R_9)_2$, wherein the two substituents R_9 are independent of each other, $-C(=X)$-R_7, $-(CH_2)$-$C(=X)$-R_7, $-O$-$C(=X)$-R_7, $-(CH_2)$-O-$C(=X)$-R_7, $-S$-$C(=X)$-R_7, $-(CH_2)$-S-$C(=X)$-R_7, $-NR_9C(=X)R_7$, $-(CH_2)$-$NR_9C(=X)R_7$, $-NR_9NHC(=X)$-R_7, $-NR_9$-OR_{10}, $-(CH_2)$-NR_9-OR_{10}, $-SR_9$, $-S(=O)R_{11}$, $-S(=O)_2R_{11}$; aryl, heterocyclyl, aryloxy or heterocyclyloxy; wherein the aryl, heterocyclyl, aryloxy and heterocyclyloxy radicals are unsubstituted or, depending upon the possibilities of substitution at the ring, mono- to penta-substituted by substituents selected from the group consisting of OH, halo-

gen, CN, NO_2, SCN, $-N_3$, C_1-C_{12}alkyl, C_3-C_8cycloalkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_8alkenyl, C_2-C_8alkynyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy and phenoxy;

or, when p is 1, R_2 together with R_3 is a bond;

or R_2 together with R_4 is =O or =S;

or R_2 together with R_4 form with the carbon to which they are bound a three- to seven-membered ring, which may be monocyclic or bicyclic, and may be saturated or unsaturated, and that may contain one or two hetero atoms selected from the group consisting of N, O and S, and which is either unsubstituted or independently of one another mono- to pentasubstituted with substituents selected from OH, =O, SH, =S, halogen, CN, $-N_3$, SCN, NO_2, aryl, C_1-C_{12}alkyl, C_3-C_8cycloalkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_8alkenyl, C_2-C_8alkynyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy, phenoxy, phenyl-C_1-C_6alkyl; $-N(R_9)_2$, wherein the two R_9 are independent of each other; C_1-C_6alkylsulfinyl, C_3-C_8cycloalkylsulfinyl, C_1-C_6haloalkylsulfinyl, C_3-C_8halocycloalkylsulfinyl, C_1-C_6alkylsulfonyl, C_3-C_8cycloalkylsulfonyl, C_1-C_6haloalkylsulfonyl and C_3-C_8halocycloalkylsulfonyl; or

or, when p is 0, R_2 together with R_4 and R_6 is ≡N;

or when p is 0, R_2 together with R_6 is $=NOR_9$ or $=NN(R_9)_2$, wherein the two substituents R_9 are independent of each other;

R_3 is H, C_1-C_{12}-alkyl, halogen, halo-C_1-C_2alkyl, CN, $-N_3$, SCN, NO_2, C_3-C_8cycloalkyl unsubstituted or substituted by from one to three methyl groups, C_3-C_8halocycloalkyl, C_1-C_{12}alkoxy, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy-C_1-C_6alkyl, C_3-C_8cycloalkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_3-C_8cycloalkylthio, C_1-C_{12}haloalkylthio, C_1-C_{12}alkylsulfinyl, C_3-C_8cycloalkylsulfinyl, C_1-C_{12}haloalkylsulfinyl, C_3-C_8halocycloalkylsulfinyl, C_1-C_{12}alkylsulfonyl, C_3-C_8cycloalkylsulfonyl, C_1-C_{12}haloalkylsulfonyl, C_3-C_8halocycloalkylsulfonyl, C_2-C_8alkenyl, C_2-C_8alkynyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy, $-N(R_9)_2$, wherein the two substituents R_9 are independent of each other, aryl, heterocyclyl, aryloxy or heterocyclyloxy; wherein the aryl, heterocyclyl, aryloxy and heterocyclyloxy radicals are unsubstituted or, depending upon the possibilities of substitution at the ring, mono- to penta-substituted by substituents selected from the group consisting of

halogen, CN, NO_2, C_1-C_{12}alkyl, C_3-C_8cycloalkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_8alkenyl, C_2-C_8alkynyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyl and C_3-C_{12}haloalkynyloxy;

or when p is 1, R_3 together with R_2 is a bond;

R_4 is H, C_1-C_{12}-alkyl, C_1-C_{12}-haloalkyl, C_1-C_{12}-hydroxyalkyl, OH, halogen, NO_2, CN, C_3-C_8cycloalkyl unsubstituted or substituted by from one to three methyl groups, C_3-C_8halocycloalkyl, C_1-C_{12}alkoxy, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_6alkoxy--C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_{12}alkenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_2-C_{12}alkynyl, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy, -P(=O)(OC_1-C_6alkyl)$_2$, -Si(C_1-C_6alkyl)$_3$, -(CH_2)-Si(C_1-C_6alkyl)$_3$, -Si(OC_1-C_6alkyl)$_3$, -N(R_9)$_2$, -(CH_2)-N(R_9)$_2$, wherein the two substituents R_9 are independent of each other, -C(=X)-R_7, -(CH_2)-C(=X)-R_7, -O-C(=X)-R_7, -(CH_2)-O-C(=X)-R_7, -S-C(=X)-R_7, -(CH_2)-S-C(=X)-R_7, -NR_9C(=X)R_7, -(CH_2)-NR_9C(=X)R_7, -NR_9NHC(=X)-R_7, -NR_9-OR_{10}, -(CH_2)-NR_9-OR_{10}, -SR_9, -S(=O)R_{11}, -S(=O)$_2R_{11}$; aryl, heterocyclyl, aryloxy or heterocyclyloxy; wherein the aryl, heterocyclyl, aryloxy and heterocyclyloxy radicals are unsubstituted or, depending upon the possibilities of substitution at the ring, mono- to penta-substituted by substituents selected from the group consisting of OH, halogen, CN, NO_2, C_1-C_{12}alkyl, C_3-C_8cycloalkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_8alkenyl, C_2-C_8alkynyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy and phenoxy;

or R_4 together with R_2 forms =O or =S;

or when p is 1, R_4 together with R_5 is a bond;

or, when p is 0, together with R_2 and R_6 is ≡N;

R_5 and R_6 independently of each other are H, C_1-C_{12}-alkyl, -N_3, CN, NO_2, OH, SH, halogen, halo-C_1-C_2alkyl, C_3-C_8cycloalkyl unsubstituted or substituted by from one to two methyl groups, C_3-C_8halocycloalkyl, C_1-C_{12}alkoxy, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy-C_1-C_6alkyl, C_3-C_8cycloalkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}haloalkylthio, C_2-C_8alkenyl, C_2-C_8alkynyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy, -P(=O)(OC_1-C_6alkyl)$_2$, -CH_2-P(=O)(OC_1-C_6alkyl)$_2$, -Si(OC_1-C_6alkyl)$_3$, -N(R_9)$_2$, -O-N(R_9)$_2$, wherein the two substituents R_9 are independent of each other, -C(=X)-R_7, -O-C(=X)-R_7, -S-C(=X)-R_7, -NR_9C(=X)R_7, -NR_9NHC(=X)-R_7,

$-NR_9-OR_{10}$, $-SR_9$, $-S(=O)R_{11}$, $-S(=O)_2R_{11}$, aryl, aryloxy, benzyloxy, $-NR_9$-aryl, heterocyclyl, heterocyclyloxy, $-NR_9$-heterocyclyl, $-CH_2$-aryl, $-CH_2$-O-aryl, $-CH_2-NR_9$-aryl, $-CH_2$-heterocyclyl, $-CH_2$-O-heterocyclyl and $-CH_2-NR_9$-heterocyclyl; wherein the aryl, aryloxy, benzyloxy, $-NR_9$-aryl, heterocyclyl, heterocyclyloxy and $-NR_9$-heterocyclyl radicals are unsubstituted or, depending upon the possibilities of substitution at the ring, mono- to penta-substituted by substituents selected from the group consisting of OH, =O, SH, =S, halogen, CN, NO_2, C_1-C_{12}alkyl, C_3-C_8cycloalkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_8alkenyl, C_2-C_8alkynyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy, phenoxy, methylenedioxy, NH_2, $NH(C_1$-C_{12}alkyl), $N(C_1$-C_{12}alkyl)$_2$ and C_1-C_6alkylsulfinyl; or

R_5 and R_6 are, together with the carbon atom to which they are bound, a five- to seven-membered ring, which may be saturated or unsaturated, and which may contain one or two members selected from the group consisting of O, NR_8 and S; and which is optionally substituted with one to three substituents selected from C_1-C_{12}-alkyl, CN, NO_2, OH, halogen, halo-C_1-C_2alkyl, C_3-C_8cycloalkyl C_3-C_8halocycloalkyl, C_1-C_{12}alkoxy, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy-C_1-C_6alkyl, C_3-C_8cycloalkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_3-C_8cycloalkylthio, C_1-C_{12}haloalkylthio, C_2-C_{12}alkenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_2-C_{12}alkynyl, C_3-C_{12}haloalkynyl and C_3-C_{12}haloalkynyloxy;

or when p is 1, R_5 together with R_4 is a bond;

or, when p is 0, R_6 together with R_2 and R_4 is $\equiv N$;

R_7 is H, OH, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_2-C_{12}alkenyl, C_2-C_{12}alkynyl, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_6 alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy, C_2-C_8alkenyloxy, $-N(R_8)_2$, wherein the two R_8 are independent of each other; aryl, aryloxy, benzyloxy, heterocyclyl or heterocyclyloxy; and wherein the aryl, aryloxy, benzyloxy, heterocyclyl, heterocyclyloxy radicals are unsubstituted or, depending upon the possibilities of substitution at the ring, mono- to penta-substituted by substituents selected from the group consisting of halogen, CN, NO_2, C_1-C_{12}alkyl, C_3-C_8cycloalkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_8alkenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy and C_2-C_8alkynyl;

R_8 is H, C_1-C_6alkyl, which is optionally substituted with one to five substituents selected from the group consisting of halogen, C_1-C_6alkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy, C_2-C_{12}alkenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_2-C_{12}alkynyl, C_3-C_{12}haloalkynyl,

C_3-C_{12}haloalkynyloxy, hydroxy and cyano; C_3-C_8-cycloalkyl, aryl, benzyl or heteroaryl; wherein the aryl, benzyl and heteroaryl radicals are unsubstituted or, depending on the possibilities of substitution on the ring, mono- to trisubstituted by substituents selected from the group consisting of OH, halogen, CN, NO_2, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_2-C_{12}alkenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_2-C_{12}alkynyl, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy and C_1-C_{12}haloalkylthio;

R_9 is H, C_1-C_6alkyl, C_1-C_6cycloalkyl, C_1-C_6alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkoxy-C_1-C_6alkyl, C_2-C_{12}alkenyl, C_2-C_{12}alkynyl, benzyl, aryl, heteroaryl;

R_{10} H, C_1-C_6alkyl, which is optionally substituted with one to five substituents selected from the group consisting of halogen, C_1-C_6alkoxy, NO_2, hydroxy and cyano; C_1-C_{12}haloalkyl, C_2-C_{12}alkenyl, C_2-C_{12}haloalkynyl, C_2-C_{12}haloalkenyl, C_2-C_{12}alkynyl, C_3-C_8-cycloalkyl, aryl, benzyl or heteroaryl; wherein the aryl, benzyl and heteroaryl radicals are unsubstituted or, depending on the possibilities of substitution on the ring, mono- to trisubstituted by substituents selected from the group consisting of OH, halogen, CN, NO_2, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_2-C_{12}alkenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_2-C_{12}alkynyl, C_3-C_{12}haloalkynyl and C_3-C_{12}haloalkynyloxy;

R_{11} is H, C_1-C_6alkyl, which is optionally substituted with one to five substituents selected from the group consisting of halogen, C_1-C_6alkoxy, hydroxy and cyano; -$N(R_9)_2$, wherein the two substituents R_9 are independent of each other; C_3-C_8cycloalkyl, C_3-C_8halocycloalkyl, C_2-C_{12}alkenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_2-C_{12}alkynyl, C_3-C_{12}haloalkynyl, C_3-C_{12}haloalkynyloxy, aryl, benzyl or heteroaryl; wherein the aryl, benzyl and heteroaryl radicals are unsubstituted or, depending on the possibilities of substitution on the ring, mono- to trisubstituted by substituents selected from the group consisting of OH, halogen, CN, NO_2, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_1-C_{12}haloalkoxy, C_1-C_{12}alkylthio, C_1-C_{12}haloalkylthio, C_2-C_{12}alkenyl, C_2-C_{12}haloalkenyl, C_2-C_{12}haloalkenyloxy, C_2-C_{12}alkynyl, C_3-C_{12}haloalkynyl and C_3-C_{12}haloalkynyloxy;

X is O or S;

or, if appropriate, an E/Z isomer, E/Z isomer mixture and/or tautomer thereof, in each case in free form or in salt form.

2. A pesticide which contains at least one compound of the formula (I) as described in claim 1 as active compound and at least one auxiliary.

3. A method for controlling pests wherein a composition as described in claim 2 is applied to the pests or their habitat.

4. A process for preparing a composition as described in claim 2 which contains at least one auxiliary, wherein the active compound is mixed intimately and/or ground with the auxiliary(s).

5. The use of a compound of the formula (I) as described in claim 1 for preparing a composition as described in claim 2.

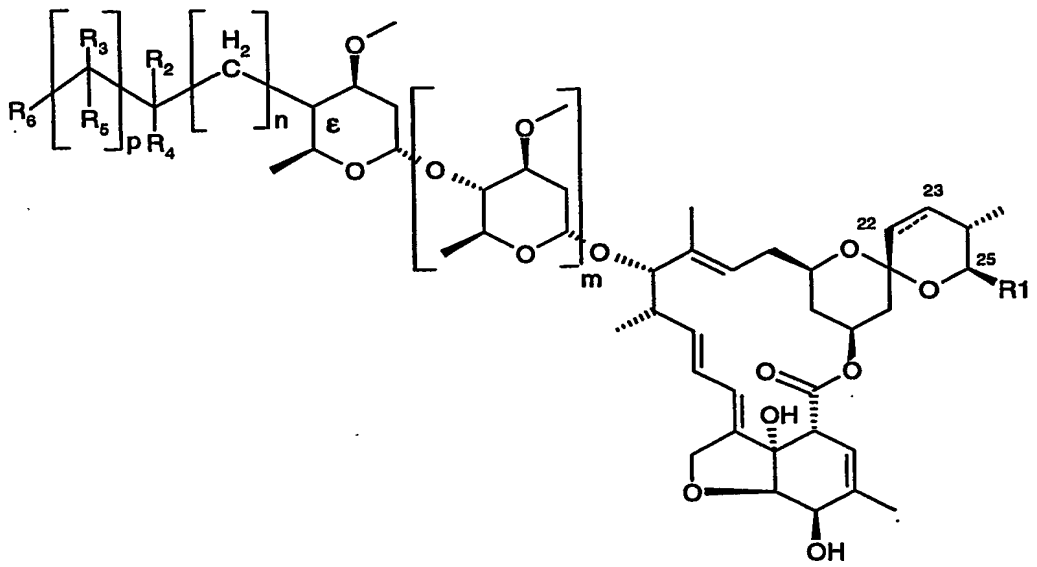
6. The use of a composition as described in claim 2 for controlling pests.

7. A method according to claim 3 for protecting plant propagation material, wherein the propagation material or the location where the propagation material is planted is treated.

8. Plant propagation material treated in accordance with the method described in claim 7.

Abstract

What is described are a compound of the formula



(I),

wherein the bond of atoms C_{22} and C_{23} is a single or double bond;

m is 0 or 1;

n is 0, 1 or 2;

p is 0 or 1;

R_1 is C_1-C_{12}-alkyl, C_3-C_8-cycloalkyl or C_2-C_{12}-alkenyl;

R_2 is for example H, C_1-C_{12}-alkyl, C_1-C_{12}-haloalkyl or C_1-C_{12}-hydroxyalkyl;

or together with R_4 form with the carbon to which they are bound for example a three- to seven-membered ring;

R_3 is for example H, C_1-C_{12}-alkyl, halogen, halo-C_1-C_2alkyl, CN, NO_2 or C_3-C_8cycloalkyl;

R_4 has the same meanings as R_2;

R_5 and R_6 independently of each other are for example H, C_1-C_{12}-alkyl, CN, NO_2, OH, SH, halogen, halo-C_1-C_2alkyl or C_3-C_8cycloalkyl;

or, if appropriate, an E/Z isomer, E/Z isomer mixture and/or tautomer thereof, in each case in free form or in salt form

a process for preparing and using these compounds and their tautomers; pesticides whose active compound is selected from these compounds and their tautomers; and a process for preparing these compounds and compositions, and the use of these compounds and compositions.